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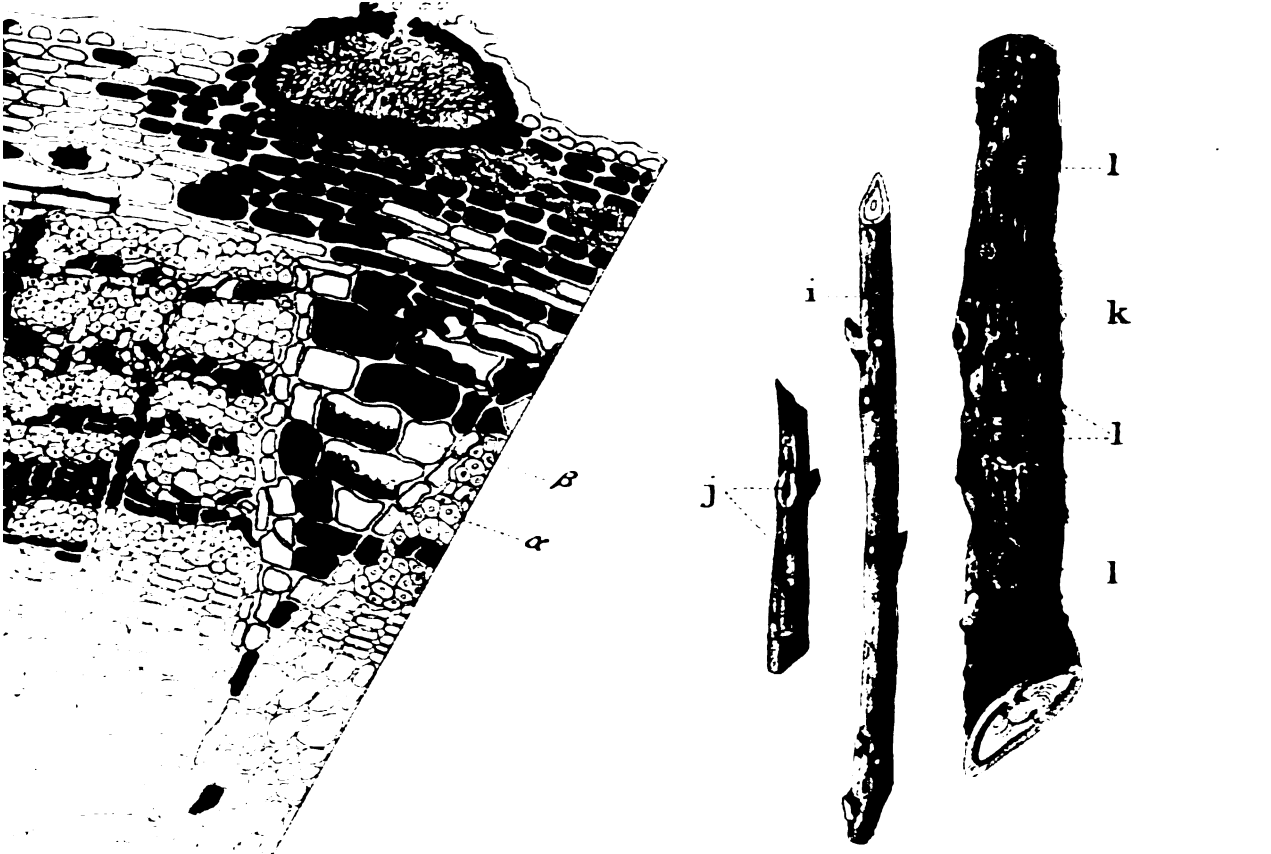

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday May 26, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 Mei 1900 Dl. IX).

CONTENTS: "On the composition of the vapour-phase in the system: Water-Phenol, with one or with two liquidphases." By Dr. F. A. H. SCHREINEMAKERS (Communicated by Prof. J. M. VAN BEMMELEN), p. 2. — "Echinopsine, a new crystalline vegetable base." By Dr. M. GRESHOFF (Communicated by Prof. A. P. N. FRANCHIMONT), p. 11. — "On the relation between radiation and molecular attraction". By J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS), p. 27. — "Plumieride and its identity with Agoniadine". By Prof. A. P. N. FRANCHIMONT, p. 35. — "On the crystallised constituent of the essential oil of Kaempferia Galanga L.". By Dr. P. VAN ROMBURGH, p. 38. — "On the durability of the agglutinative substances of the bloodserum". By Dr. J. E. G. VAN EMDEN (Communicated by Prof. TH. H. MAC GILLAVRY), p. 41. — "The amount of the circulation of the carbonate of lime and the age of the Earth". I. By Prof. EUG. DUBOIS (Communicated by Prof. J. M. VAN BEMMELEN), p. 43. — "The solubility of Calcium Carbonate in Sea-water". By Dr. ERNST COHEN and H. RAKEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 63. — "On the phenomena of condensation in mixtures in the neighbourhood of the critical state". By Dr. CH. M. A. HARTMAN (Communicated by Prof. H. KAMERLINGH ONNES), p. 66. — "Measurements on the magnetic rotation of the plane of polarisation in liquefied gases under atmospheric pressure". By Dr. L. H. SIERTSEMA (Communicated by Prof. H. KAMERLINGH ONNES), p. 70. (With one plate). — "A new method for the exact determination of the elevation of the Boiling-point". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 74. — "Thermodynamics of Standard Cells" (2nd part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 74. — "On the Enantiotropy of Tin". V. By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 74. — "The formation of mixture-crystals of Thalliumnitrate and Thalliumiodide". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 74.

The following papers were read:

Chemistry. — *"On the composition of the vapour-phase in the system Water-Phenol, with one and with two liquid-phases".* By Dr. F. A. H. SCHREINEMAKERS (Communicated by Prof. J. M. VAN BEMMELEN).

(Read April 21, 1900.)

1. *The apparatus.*

To determine the composition of the vapour phases the apparatus shown in fig. 1 was used. The flash *A* into which the mixture to

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be investigated was introduced is closed by means of a ground in tube *B* containing a little mercury in which the thermometer was placed.

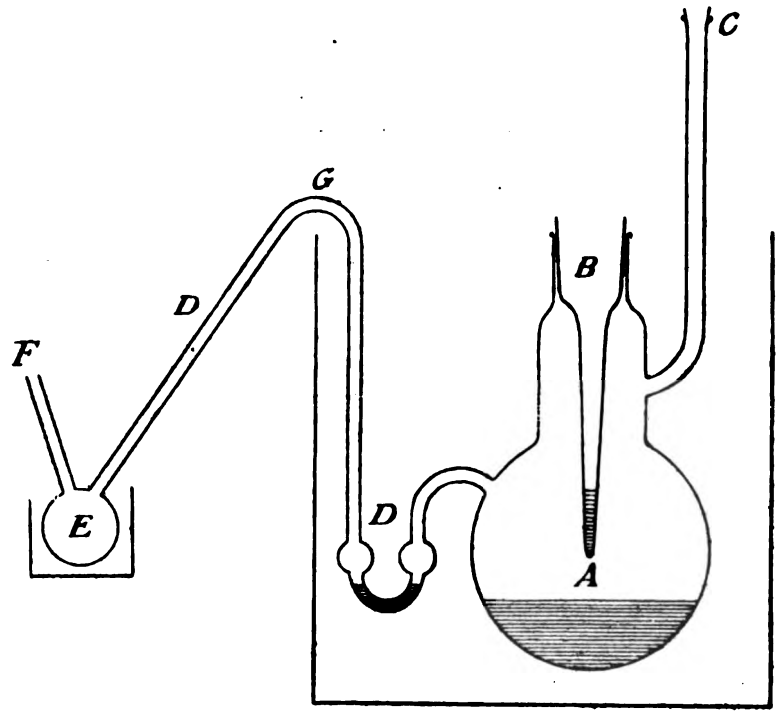

Fig. 1.

The tube *C* is connected by means of a ground joint with the condenser and through this with a space of about 18 litres capacity, in which the pressure can be altered as desired by means of a pump; the pressure in this space was determined by means of an open mercury-manometer.

The flash *A* is further connected by means of the tube *D* with the little flask *F* which is connected by a ground joint with *D*. This flask may further be connected by means of *F* with the outer air, or with the space with which *A* is always connected or with another space in which the pressure may be regulated at will. In order to determine the vapour tension at a certain temperature, the bath was raised a few degrees above the desired temperature and the pressure in the space which is connected with *A*, afterwards altered, until the liquid contained in *A* began to boil. By a further slow change of the pressure, the boiling point of the liquid was brought to the desired temperature and read off on the thermometer placed in *B*.

The vapour evolved in *A* ascends through *C* into the condenser,

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where it is condensed and returned to A; it cannot pass into the space E, because the tube D contains a little mercury between the two small bulbs, and the space E is connected with the same space as A.

To determine the composition of the vapour phase, some vapour from A was transferred to the flask E, which was placed in a freezing mixture in order to completely condense the vapour. In order to transfer the vapour from A to E the latter was connected, by means of the tube F, with a space in which the pressure was a little less than that in the space connected with A. The vapour evolved in A now bubbles through the mercury in the tube D; the rapidity with which this takes place may be regulated at will by making the difference in pressure between A and F greater or smaller. By means of this arrangement, it is not only possible to regulate the rate at which the vapour is conveyed from A to E, but also to stop or to restart the transference at will, the temperature and pressure in A remaining unchanged. Because the bath has always a higher temperature than the liquid and vapour in A, no condensation can take place in that part of the tube D which is immersed in the bath, but condensation may occur in the part of the tube which is outside the bath. To prevent condensation at G this part of the tube was maintained at a higher temperature by means of a small flame; the vapour which condensed in the further end of D, was transferred to E by heating after the distillation was ended.

The composition of the liquid remaining in A was, of course, altered by the removal of vapour; as, however a quantity of 100—200 grams was introduced into A and only 5—10 grams of liquid condensed in E, the change in A was as a rule comparatively small, unless the vapour- and liquid-phases differed very much in composition. In such cases I give the composition of the liquid-phase both at the beginning and the end.

During the transfer of vapour from A to E, vapour was continually rising into the condenser where it was condensed. This condensed liquid, the composition of which was, of course, in general different from that of the liquid in A, gave off a different vapour when flowing down the sides and so caused an error. As a rule, however, this error will doubtless be small. Some determinations have been repeated without admitting any vapour into the condenser during the transfer from A to E. For this purpose a little apparatus was used by means of which the tube C could be closed and reopened below the level of the bath. The use of this apparatus, however, gave rise to many difficulties and it was therefore only used a few times.

As experience showed, the determinations of the vapour tension

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are not quite correct but may be wrong to the extent of a few m.m.; this was found by repeating several times the determination of the vapour-tension of pure water or of a three-phase system in the same apparatus at the same temperature and with the same thermometer, when the determinations sometimes differed among themselves to the extent of 2 or 3 m.m. The liquid collected in the flask E was at the end of the operation weighed and analysed. In the system Water-Phenol, the phenol was estimated by the method of KOPPESCHAAR, i. e. by titration with a solution of K Br and K Br O_3.

II. *The three-phase system.*

In the system: Water-Phenol, three phases can be in equilibrium with each other between the transition-temperature (about 1°5) and the critical temperature (about 68°), namely two liquid-phases and the vapour. The composition of the two liquid-phases, which may be in equilibrium with each other at the different temperatures, has already been investigated several times, among others, by ALEXEJEFF [1]) and V. ROTHMUND [2]); I have now determined the composition of the vapour-phase in the way described.

In table I T stands for temperature; P for the pressure of the three-phase system in m.m.; L_1 L_2 and L_v for the composition of the three phases, L_1 and L_2 for those of the two liquids and L_v for that of the vapour. The composition is expressed in percentage by weight of phenol in the mixture of phenol and water.

TABLE I.

T	P	L_1	L_2	L_v
29.°8	29	8	70	5.96
38.°2	48	9.5	67	6.98
42.°4	62	10	66	6.91
50.°3	94	12	63	7.28
56.°5	126	14.5	60	7.83
60.°1	150	17	57	8.06
64.°4	182	22 5	48	8.66

The composition of the three phases is shown graphically in figure 2; the temperature is measured along the horizontal axis, the pressure along the vertical axis. The lines L_1 and L_2 represent

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[1]) Wied. Ann. 28. 305.

[2]) Zeitschr. f. Ph. Ch. 26. 433.

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the two liquid-phases, the line L_v the vapour-phase. It will be seen from the figure, that the two liquid-phases L_1 and L_2 gradually approach the same composition as the temperature rises, and that at 68° they become identical at a point k which indicates about 34 pCt. of phenol. The line L_v, which shows the vapour phases, which may be in equilibrium with both the liquid-phases, lies entirely below the line L_1. The vapour-phase, therefore contains less phenol than occurs in either of the other liquid-phases.

If we call L_1, which contains the most water, the aqueous, and L_2, which contains the most phenol, the phenol-layer, then the vapour contains still less phenol than the aqueous layer.

If a mixture of two liquid-phases of water and phenol is distilled at a constant temperature, say 56°.5, then according to the preceding table the vapour pressure is 126 m.m.; the aqueous layer then contains 14,5 pCt. of phenol, the phenol-layer on the other hand 60 pCt., whilst the vapour only contains 7,83 pCt. of phenol. The aqueous layer has, therefore, a composition between that of the vapour and the phenol-layer; on distillation the aqueous layer will be resolved into the phenol-layer and the vapour, its volume decreasing continually until finally only the phenol-layer remains in the retort. If now the distillation is pushed further at constant T, the pressure cannot longer remain constant, but it must fall as there are now only two phases remaining instead of three. I will revert to this matter presently.

The vapour-curve L_v has in this system, a position *outside* the two liquid-curves L_1 and L_2. In other systems it may, however, be situated between them; this is for instance the case with the system Water-Aniline which I will mention later on.

It is plain that the different position of branch L_v may give rise to other phenomena during the distillation of two liquid phases. This will be discussed subsequently.

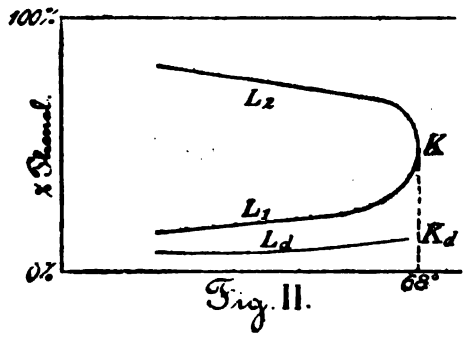

Fig. II.

In Figure 2, the pressure has not been included; this might be done by introducing a third axis perpendicular on the plane of the drawing and marking on this the pressure. The lines L_1 L_2 and L_v then no longer lies in the plane of the drawing, but in space, in such a way that their three projections on the plane P—T form a curved line.

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This line on the plane P—T shows the relation between the temperature and the pressure of the three-phase system. It is, according to table 1, a line which rises with the temperature.

III. *The two-phase system.*

The different two-phase systems which may appear in a binary system, leaving solid phases out of account, are:

1st The system of two liquid-phases.

2nd The system of a liquid with vapour.

The first system has been investigated by VAN DER LEE [1]); he determined the influence of the increase in pressure on the lines L_1 and L_2, and found it to be very small.

I have now examined the second system, mainly in order to discover the connection between the composition of the liquid and the vapour. This may be done in two widely different ways; first the boiling-points and the compositions of the vapours of liquids of different composition may be determined at a constant pressure; secondly the vapour-pressure and composition may be determined at a constant temperature. I have chosen the last method at the temperatures 56°3, 75° and 90°. The first temperature is situated below the critical point; two liquid phases therefore make their appearance; at the two other temperatures this is not the case.

The following table contains the determinations at 56°.3.

TABLE 2.

N°.	L	D	P
1	0 pCt.	0 pCt.	125 mm.
2	2.0	2.55	125
3	5.58	5.49	127
4	7.42	6.57	126.5
5	10.88	7.42	127
6	14.5—60	7.83	126
7b	69.2	9.88	124
7e	76.7		122
8b	80.34	11.98	118
8e	88.06		102

The percentage of phenol in the liquid is given under L; the composition of the vapour under D, and the vapour pressure under P.

Determination N°. 6 relates to the *two* liquid-phases which may

[1]) Dissertation. Amsterdam.

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be in equilibrium with each other at 56°.3, one of which contains 14.5 pCt., the other 60 pCt. of phenol.

Determination N°. 7 is entered under 7^b and 7^e ; 7^b gives the initial, 7^e the final concentration of the liquid. As will be seen, these differ by 7.5 pCt., whilst the vapour differs immensely in composition from the liquid.

The same applies to determination 8.

As will be seen from the table, a liquid containing about 5.5 pCt. of phenol yields a same composition. Liquids containing less than 5.5 pCt. of phenol yield a vapour containing more phenol than the liquid; liquids containing more phenol, however, yield a vapour containing less phenol.

Table 3 gives the determination at 75°.

TABLE 3.

No.	L	D	P
1	0	0	289
2	2.43	3.44	293
3	4.15	5.21	293
4	7.51	7.41	294
5	16.82	9.11	294
6^b	22.53	9.36	294
6^e	24.18		294
7^b	44.44	9.85	294
7^e	49.2		294
8^b	60.47	10.43	292-293
8^e	65.75		± 289
9^b	76.7	12.63	280
9^e	82.4		259
10^b	88.06	21.37	218
10^e	91.7		177

In determination N° 4, the vapour and liquid have again about the same composition; with a percentage of 7.2 of phenol they are identical.

If therefore a liquid containing less than 7.2 pCt. of phenol is distilled at 75°, the vapour contains more phenol than the liquid; the reverse is the case if the liquid contains more than 7.2 pCt. of phenol.

The determinations at 90° are given in table 4.

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TABLE 4.

N°.	L	D	P
1	0	0	525 mM.
2	2.36	3.64	528
3	7.00	7.69	531
4	8.29	8.30	531
5	9.74	8.96	530
6^b	17.4	10.40	530
6^e	20.4		530
7^b	33.6	10.78	530
7^e	35.0		530
8^b	42.2	10.87	530
8^e	44.2		530
9^b	56.3	11.24	530
9^e	58.0		530

As shown in this table, the liquid which at this temperature is in equilibrium with a vapour of the same composition contains about 8.29 pCt. of phenol.

The results shown in the first three tables may be represented graphically in different ways.

I will here, however, make use of only one of these, namely that showing the composition of the vapour-phase as a function of the liquid. The vapour-pressure is thus not considered.

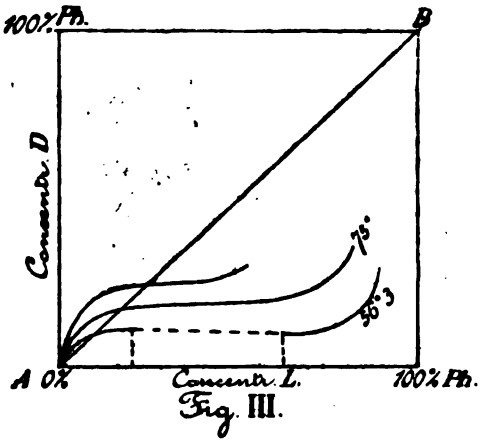

Fig. III.

Figure 3 is a graphical representation of this kind; the concentration of the liquid is measured along the horizontal axis, that of the vapour (in percentage of phenol) along the vertical axis.

If we draw the line AB through the square, the points on it represent liquids whose vapour has the same composition. If a point is situated to the left of AB, the vapour contains more phenol than the liquid; if to the right it contains less phenol.

From the drawing it is seen that at each of the three temperatures, a liquid containing a small quantity of phenol yields a vapour containing more, and one containing much phenol yields a vapour containing less phenol than itself.

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The point of intersection of a curve with AB represents a liquid which is in equilibrium with a vapour of its own composition. The proportion of phenol in this liquid increases with the temperature. This liquid must have a maximum or a minimum vapour pressure; in our case a maximum one.

In our case, according to table 2, the maximum must be at N°. 3 namely 127 m.m.; in No. 4 the vapour-pressure is certainly not quite accurate, as N°. 5 again indicates 127 m.m. The deviation is, however, far within the experimental error which may amount to several mm. That, in figure 3, the line of 56.3° ends, at least experimentally, in the points L_1 and L_2 is clear, because L_1 and L_2 indicate the composition of the two liquid-phases which are in equilibrium with the vapour. If, therefore, water and phenol are brought together in such a proportion, that the mixture is represented by a point situated between L_1 and L_2, this will break up at 56°3 into the two liquid-phases L_1 and L_2 and vapour, the concentration of which is indicated by the ordinate of one of these points.

In the two other curves the straight line L_2 L_1 does not occur; they belong to temperatures above the critical point. They, however, present the peculiarity, that they are almost horizontal for a considerable distance; or in other words — as may also be seen from the tables 3 and 4 — when the liquid has reached a certain percentage of phenol the composition of the vapour is but little affected even by considerable variations in the amount of phenol in the liquid. According to table 3, the vapour at 75°0 only changes from 9.11 to 10.43 pCt. of phenol, when the liquid changes from 16.82 to 65.75 pCt. With a still larger percentage of phenol in the liquid the amount of phenol in the vapour increases more rapidly, finally increasing very fast indeed, since all the lines in figure 3 must terminate at B.

Not only the amount of phenol contained in the vapour, but also the vapour-pressure alters but little, when the composition of the liquid varies between very wide limits.

In table 3 the maximum of vapour-pressure must lie between the two determinations 3 and 4 and very close to N°. 4. In determinations 4, 5, 6 and 7, the vapour pressure is constant at 294 m.m.; theoretically this is, of course, impossible, but experimentally the differences may fall quite within the limits of experimental errors.

VAN DER LEE has also measured the vapour pressure at 75°; he also finds a vapour-pressure of 294 mm. when working with a liquid of widely varying concentration. His other determinations agree fairly well with my own; only liquids containing a very large amount

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of phenol show differences. As I have now determined the composition of liquid and vapour, it is possible to test the observations by means of the approximately accurate formula of VAN DER WAALS:

$$\frac{dP}{dx_d} = \frac{P\,(x_d - x_l)}{x_d\,(1 - x_d)}.$$

The best way would be to take the values of x_d and P from the determinations as also the values of $\frac{dP}{dx_d}$, and then to calculate x_l by means of the formula and compare this value with the experimental result. In our case, however, $\frac{dP}{dx_d}$ cannot accurately be deduced from the experiments, as P does not change or very little between very wide limits.

I have therefore, followed a different plan and calculated $\frac{dP}{dx_d}$ by means of the experimental values of P, x_d and x_l from the formula. For this purpose let us take the determinations at 75° (table 3) and recalculate everything in molecules; let us then take the mean of the initial and final compositions and pressures in experiments 7, 8, 9 and 10. We then obtain:

TABLE 5.

N°	x_l	x_d	$x_d - x_l$	P	$\frac{dP}{dx_d}$
1	0	0	0	289	
2	0.0047	0.0067	+0.0020	293	+ 88
3	0.0082	0.0104	+0.0022	293	+ 62
4	0.0153	0.0151	−0.0002	294	− 3
5	0.0372	0.0188	−0.0184	294	− 294
6	0.0551	0.0193	−0.0358	294	− 556
7	0.1446	0.0204	−0.1242	294	−1825
8	0.2477	0.0218	−0.2259	291	−3083
9	0.4296	0.0269	−0.4027	270	−4154
10	0.6322	0.0493	−0.5829	197	−2449

From the values of $\frac{dP}{dx_d}$ in the preceding table I have calculated the values of ΔP for each pair of successive observations.

Considering for example observations 2 and 3, the value of $\frac{dP}{dx_d}$ may be regarded as the mean of the values found in the two exper-

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iments, i. e. $\frac{88 + 62}{2} = 75$; the value of ΔP between observations 2 and 3 is therefore,

$$\Delta P = \Delta x_d \frac{dP}{dx_d} = (0.0104—0.0067) \times 75 = 0.35 .$$

The values of $\frac{dP}{dx_d}$ and ΔP thus obtained are given in table 6; also, for comparison, the values of ΔP obtained by direct experiment.

TABLE 6.

Between observations	$\frac{dP}{dx_d}$	ΔP calculated	ΔP found
No. 2 and No. 3	75	0.3 m.M.	0 m.M.
3 » 4	30	0.1	1
4 » 5	— 149	— 0.5	0
5 » 6	— 425	— 0.2	0
6 » 7	— 1190	— 1.3	0
7 » 8	— 2454	— 3.4	— 3
8 » 9	— 3618	— 18.5	— 21
9 » 10	— 3302	— 73.9	— 73

As may be seen from the table, ΔP calculated and ΔP found agree satisfactorily; the difference are smaller than the experimental errors which may amount to several m.ms.

Chemistry. — "*Echinopsine, a new crystalline vegetable base*". By Dr. M. GRESHOFF (Communicated by Prof. A. P. N. FRANCHIMONT).

(Read April 21, 1900).

Of late years alkaloids have been discovered in plantfamilies which, previously, had been made but little the subject of phyto-chemical studies, and in which, at any rate, no vegetable bases had been found or even suspected. So, for instance, in the large family of the *Compositae*, which comprises about one-tenth part of all the phanerogamia, with more than 800 genera.

The writer has been engaged for many years in the systematic study of alkaloidal distribution in plants, also in this family, [1]) and

[1]) Compare: *On the distribution of alkaloids in the family of the Compositae.* Ned. Tijdschr. v. Pharm., Mei 1900, blz. 137. In this article 50 alkaloid-containing genera are summarised, mostly the result of my own investigations.

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has now the opportunity to present the meeting with at least one of his new compositae-alkaloids in a pure condition, and to give a description of the same.

First of all, some particulars about the botanical origin.

The genus *Echinops* L. (= *Echinanthus* NECK., *Echinopus* TOURN., *Sphaero cephalus* L.) belongs to the division *Tubuliflorae-Cynareae* of the Compositae. These *Cynareae* are divided into four groups: *Echinops*, *Carlina*, *Carduus* and *Centaurea*, all plants popularly known as thistles; some are characterised, from a chemical standpoint, by containing alkaloids, glucosides, bitter principles and pigments; a few yield hydrocyanic acid.

The group *Echinops* only contains this genus itself, and *Acantholepis orientalis* LESS., a plant from the steppes of Central-Asia. *Echinops* numbers about 60 species, also mostly Central-Asiatic herbs with alternate, frequently thorned leaves, and all species characterised by having capitula. To the West, the *Echinops* territory extents over the whole of the South of Europe and the coasts of the Mediterranean, to the East as far as Japan; some species are also natives of tropical Africa. In Germany, *E. sphaerocephalus* L. grows wild; no species is found wild in Holland. In that country various kinds are, however, cultivated as ornamental plants, on account of the robust stature and the beautiful large flower heads from which the genus derives its name of "ballthistle" (the latin name is composed of *echinus*, hedgehog and *ops*, eye or appearance). The flowers are sometimes light blue *E. Ritro* L., or dark blue *E. bannaticus* ROCH. The genus is divided by botanists into 7 sections; compare ENGLER u. PRANTL, *Natürliche Pflanzenfamilien* IV, 5, p. 313. The species are mostly described in BOISSIER's *Flora orientalis* and also by BUNGE, *Bull. de l'Académie de St. Pétersbourg* VI, 390. My investigation extents over 15 species from different sections [1]) which all were found to contain echinopsine, so that there is reason to believe that the presence of this alkaloid is a general characteristic of the *Echinops*-species.

On the use of *Echinops* in popular medicine and in toxicology, a question revived by the discovery of the powerful Echinopsine, not much information is at my disposal. Different species, such as *E. Ritro* L., *dahuricus* FISCH.,

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[1]) This is perhaps the proper place to state the source of the important material of my investigation and to thank those who provided me with the same. From the botanical garden at Leiden, I received through the care of Mr. E. TH. WITTE, hortulanus, *E. Ritro* L. and *E. niveus* WALL. Of the first plant, the firm HAAGE u. SCHMIDT at Erfurt provided me with the 10 kilograms fruits, which have served for the preparation of a larger quantity of echinopsine, than the supply from the botanical garden allowed. I also got from the same source *E. sphaerocephalus* L., *E. exaltatus* SCHRAD., *E. paniculatus* JACQ. and *E. syriacus* BOISS. On a holiday tour in Sweden in Aug. 1899 I noticed in the excellently kept botanical garden of Lund and Upsala some other varieties cultivated there. In Lund, I collected leaves of *E. dahuricus* FISCH., *E. bannaticus* ROCH., *E. platylepis* TRAUTV. and *E. microcephalus* SIBTH.; afterwards I received from there seed of *E. globifer* JANKA and of another species which according to Dr. SV. MURBECK was, probably, *E. commutatus* JUR. From Lund, the hortulanus Mr. FR. PETTERSON forwarded me beautiful material from *E. viscosus* DC., *E. humilis* BIEB. and *E. elatus* BUNGE.

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sphaerocephalus L., are used in East-Russia and Siberia as diaphoretica and diuretica, are also applied in skin diseases. In olden times, the "Herba echinopsidis" was also used in Europe for treating gravel and stone. To Dr. G. VAN VLOTEN of Leiden I am indebted for a note on the use of this genus by the Arabs. IBN WAHSCHIJA states in his treatise: *De Venenis* (cod. Leiden) the following particulars about a plant which he calls "Djirdama":

"Djirdama grows at Djukha and at Schaflatha (in Babylonia), and is a powerful poison which kills quickly. It is a tall plant with small leaves, its stem attains the height of a meter. It has a white roselike flower and its taste is even more pungent than that of mustard. A person who has had 2—2,5 drachms of the pulverized plant administred in his food feels a violent itching on the surface of his body and a twisting and pains in the throat and the stomach and a violent burning, so that he often undresses and sits down naked. A weight of two "daniq's" administred in a beverage to pregnant women causes abortion, and a little of the powder rubbed on the skin causes burning and inflammation."

It is questionable whether this plant is really meant for an *Echinops*, as the description corresponds more with that of a pungent crucifer. The name, however, agrees with that of FORSKAHL, *Flora aegyptiaco-arabica*; but it must not be forgotten that FORSKAHL's names are of modern times, whilst those of IBN WAHSCHIJA date from about 800—900. It is, however, true that *Echinops* has indeed been proved to contain a rapidly killing poison, while if the last line of IBN WAHSCHIJA is intended for the pappus, this is also in complete accordance with the facts that it burns on the skin exactly like itchpowder. (*Mucuna.*)

A notice in the *Pharmacographia Indica* seems important, that *Echinops echinatus* DC. is an Indian medicinal plant, called in sanskrit "Utáti" and sold in the bazaars as "Utkátara". The root is bitter and serves as a tonic and diuretic. I may not, however, omit to state that Prof. Dr. H. KERN of Leiden does not believe Utáti to be a sanskrit word and said that *Echinops* is not to be found in literature on ancient Indian medicine. Messrs. D. HOOPER and G. WATT of Calcutta, coeditors of the said *Pharmacographia*, could not as yet give me further particulars on the subject of Utáti, but they have promised to order material of this drug for me from Mysore, to ascertain whether the action is due to echinopsine.

For the preparation of Echinopsine chiefly use has been made of the above mentioned fruits of *Echinops Ritro* L., collected for this purpose by Messrs. HAAGE and SCHMIDT of Erfurt. The first difficulty experienced with this material was its unusual bulk, which excluded the use of extraction-apparatus of ordinary size. Fully two-thirds of it was a straw-like chaff, a stiff tile-like involucrum, which could only be separated with very great difficulty from the fruit proper. A great deal of trouble was caused by the sharp hairs on the fruit, acting on the skin like itchpowder; by rubbing the fingers with oil this could be somewhat guarded against. The fruits yield $^2/_3$ of seed and $^1/_3$ of chaff, but the commercial article consists to the extent

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of one-half of empty fruits. The hard exterior (yielding 5,4 pCt. of ash) does not contain alkaloid, but yields a dark colored extract which impedes the purification of the alkaloid contained in the fruits. An aqueous decoction of the fruits tastes bitter yet at 1 : 3000—4000, but that of the involucrum is tasteless. It is, therefore, advisable to remove the involucra in order to obtain a cleaner and less bulky material, but this end cannot be attained either by crushing and grinding, or by sifting; the only way is by peeling the fruits by hand, but this is very tedious work. Under those circumstances, I have called in the aid of the governor of the penitentiary at Haarlem where this labour of separating the chaff has been performed by convicts. One kilogram crude material contains 36000 fruits and measures 10 dM^3.

The purified material (32 pCt. by weight of the original) was passed through a sieve, to remove the hairs, ground next and again sifted to retain pieces of the fruit-shell. The powdered seed boiled with 10 times its weight of alcohol of 95 pCt. yielded at the first extraction 19,2 and at the second 4 pCt. of extract, total 23,2 pCt. which high percentage is caused by the fatty oil from the seeds which has dissolved in the alcohol. The material was, therefore, first deprived of its oil by extraction with below 50° rectified petroleum ether, which does not dissolve any alkaloid. The powder may also be moistened with an equal weight of ether and then strongly pressed; nearly all the oil is thus removed with the ether. This seedcake was then dried, again pulverized and now percolated to exhaustion with alcohol of 95 pCt. mixed with 3 pCt. of acetic acid. A good yield is also obtained by boiling a few times with alcohol containing acetic acid and pressing warm each time. Of the straw-yellow tincture the alcohol was distilled off. The remnants of this extraction were only bitter at 1 : 150, being $^1/_{20}$ to $^1/_{27}$ of the original bitterness. The alcoholic extract had a peculiar ozonelike odour; it was taken up with water and filtered; remained on the filter a little of a not-bitter resin, but the filtrate was intensely bitter. This was once more shaken out with petroleum ether, a large quantity of chloroform added, the acid nearly neutralized with sodium carbonate and the whole thoroughly shaken, after the addition of an aqueous solution of caustic potash, slightly in excess. The extraction with chloroform was repeated three times; all the alkaloid goes into the solvents; after distilling off the chloroform, it remains as a light-yellow crystalline mass which dissolves readily in alcohol; the solution is strongly green fluorescent. This solution is decolorized by animal charcoal, but it retains its fluorescence, which

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property is shared by the crystals. There is, however, a liquid extremely well adapted to complete the purification of the crystalline vegetable base present in this complex; it is pure benzene. This readily dissolves the alkaloid by warming, but on cooling off separates practically all out, leaving the fluorescent admixture in solution.

In this manner, by repeated crystallisation until a substance of constant melting point is obtained and also by the judicious use of animal charcoal, a pure and unmixed chemical body is obtained, Echinopsine. This substance may also be obtained in an equally pure state by a repeated crystallisation from boiling water.

In this way 0,5 pCt. of Echinopsine was obtained from the chaff-deprived fruits of *E. Ritro*; about equally large is the yield of Echinopsine, from the fruits of other species, analysed by me, such as *E. bannaticus*, *exaltatus*, *globifer*, *niveus*, *paniculatus*, *sphaerocephalus*, *syriacus*, *viscosus*; the yield of Echinopsine from select material of *E. humilis* and *elongatus* was considerably higher; from the first named species it amounted to 1,20 pCt. (!), the other yielded 0,84 pCt. Material received from Erfurt in February 1900 also yielded quite 0,8 pCt. of Echinopsine and in addition 0,1 pCt. of Echinops-fluorescine and 0,15 pCt. of Echinopseine. The amount of alkaloid in the leaves of *E. bannaticus*, *dahuricus*, *nivalis*, *platylepis*, which like those of *E. Ritro* hardly taste bitter, does not exceed 0,01 pCt. in the fresh or 0,04 pCt. in the dry material. It is considerably higher in the leaves of *E. microcephalus*, *viscosus* and *globifer*, which are all perceptibly bitter. From the fresh roots of *E. Ritro* about 0,1 pCt. of Echinopsine may be prepared.

Echinopsine obtained by this process crystallises in thin colourless needles of several cM. in length, forming feathery groups. As has already been shown, it possesses the general properties of an alkaloid; it contains nitrogen, and leaves no ash. It is a weak base; the crystals when pressed between moist red litmus paper do not colour this blue. The melting point is exactly 152° C. When heated higher Echinopsine remains unaltered for a long time, then decomposes and burns with a sooty flame.

Echinopsine dissolves 1 : 60 in water at 15°; in boiling water it dissolves very readily 1 : 6. The alkaloid practically all separates from the saturated solution on cooling, first anhydrous; the fluid then solidifies to a snow-white mass liquifying again upon the addition of hydrochloric acid. Echinopsine dissolved in water shows very beautifully the phenomenon of supersaturation; the introduction of a minute crystal into the solution soon causes an abundant

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separation of the alkaloid. On slow evaporation, Echinopsine may be obtained in large transparent hydrated crystals; these become opaque when heated with water, before dissolving, owing to loss of water of crystallisation.

Echinopsine is easily soluble in methyl-, ethyl- and amyl-alcohol, not so easily in carbon disulphide, insoluble in petroleum ether. The base is soluble in ethyl ether when freshly precipitated, but when crystallised it requires about 600 parts of that solvent at 15°; this is the reason why ethyl ether is not suitable as an extraction liquid for Echinopsine. Chloroform is a very suitable fluid, which dissolves the alkaloid at the ordinary temperature in all proportions and leaves it in a unaltered state on evaporation. Benzene dissolves it but sparingly in the cold (15°), but easily at 80°, about 1 in 10; this fluid is, therefore, well adapted for the purification of Echinopsine. The hydrated base is soluble in benzene with much more difficulty than the anhydrous compound; addition of water to the cold solution of the latter therefore causes a further separation of alkaloid.

The solutions of Echinopsine are all colourless and do not show fluorescence, neither when acidified with sulphuric acid.

Echinopsine is optically inactive (a 2,5 pCt. alcoholic solution examined in a 10 cM. tube showed no polarisation at 15°.)

An aqueous solution of echinopsine faintly acidified with hydrochloric acid is a bitter-tasting liquid; a hypodermatical injection of 10 milligrams in a mouse proved fatal. Prof. Dr. R. KOBERT of Rostock has, at my request, closely studied the poisonous action (see Addendum I).

Echinopsine gives precipitates with phospho-molybdic acid, solution of iodine, Mayer's reagent, picric acid, tannin, mercuric chloride, gold- and platinic chloride, potassium thiocyanate, potassium ferrocyanide and potassium chromate. The delicacy of these general alkaloid-reagents is but moderately great; one drop of a solution of echinopsine $^1/_{1000}$ gives precipitates with a drop of all the said reagents; solutions of $^1/_{10000}$ only with the first five, of $^1/_{100000}$ only with the first two. Solutions of $^1/_{25000}$—$^1/_{30000}$ are to me hardly bitter; this is also the limit of the picric acid and mercuric-potassium iodide test. (Mayer's reagent).

The latter reagents are well adapted for micro-chemical reactions but an aqueous or alcoholic solution of iodine is so in a still higher degree (limit 1 : 100000); the crystalline precipitates obtained with mercuric chloride, potassium thiocyanate, potassium ferrocyanide and potassium chromate are also very useful.

The localisation of Echinopsine in the tissues may be very plainly

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traced by the aid of iodine solution which yields a beautiful *crystalline* precipitate in the cell. This study has been undertaken by Prof. Dr. ED. VERSCHAFFELT at Amsterdam, who will communicate his preliminary results in Addendum II.

Both the anhydrous and hydrated Echinopsine excel by crystallising unusually easily; from every solvent even traces of alkaloid leave a beautiful crystalline spot. The hydrated crystals belong to the rhombic system.

Echinopsine, although a weak base, is very stable.

Echinopsine does not decompose, when melted, until 350°, when it gradually chars, but even after having been heated for an hour at 450°, the liquified mass yield yet about one-third of unaltered alkaloid. Melted with potassium hydroxide it gradually forms a redlead-coloured resin, whilst ammonia is being evolved and an odour of pyridine is perceptable. Echinopsine dissolves almost colourless in mineral acids, also in sulphuric acid on adding weak or strong oxidising agents. It also yields, under circumstances to be investigated later on, particularly by the action of acids by a high temperature, a decomposition product, which may be recrystallised from water and then appears as brown hard nitrogenous crystals which still give alkaloidal reactions, may be extracted from an acid fluid, by means of chloroform, and melt at 198°.

Echinopsine has a special reaction which should not be overlooked. Moistened with a dilute solution of ferric chloride it gives a fine blood-red colour; other colour reactions have not yet been observed.

This base forms a number of salts eminently crystalline but of a loose combination; the amount of water of crystallisation is not constant.

The first combustions of the Echinops-alkaloid did not give concurring figures for carbon. The melting point was not only raised, (at first it was 140°), when the total alkaloid, however colourless, was still further purified, but the percentage of carbon (at first 73 pCt.) [1]) increased owing to the previous admixture of accompanying alkaloid closely related to Echinopsine. But even the analysis of chemically pure Echinopsine presents difficulties; this substance is extraordinarily troublesome to ignite and gives easily a too low carbon figure unless it is ignited in a current of oxygen. I will

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[1]) *Analyses of the total alkaloid*:

0,1760 gr. gave 0,4734 gr. of CO_2 and 0,0950 gr. of H_2O, therefore C. 73,4 pCt. and H 6,0 pCt.
0,1366 " " 0,3650 " " " 0,0818 " " " " 72,9 " " " 6,6 "
0,1522 " " 12,3 c.c. of N. at 13° and 765 m.m. therefore N. 9,5 pCt.

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only mention here those elementary analyses, which have been used as the base of the formula. A part of the analyses was done by Mr. J. SACK, assistant in this laboratory.

Estimation of carbon and hydrogen.

I.	0,1758	gr.	of	Echinopsine	gave	0,0950	gr.	of	H_2O	and	gr.	CO_2.
II.	0,1522	"		"	"	0,0844	"	"	"	0,4290	"	"
III.	0,2208	"		"	"	0,1194	"	"	"	0,6186	"	"
IV.	0,1196	"		"	"	0,0606	"	"	"	0,3368	"	"

therefore:

	I.	II.	III.	IV.
H.	6,0 pCt.	6,2 pCt.	6,0 pCt.	5,6 pCt.
C.	———	76,9 "	76,4 "	76,8 "

Estimation of nitrogen.

0,2100 gr. of echinopsine analysed by the Kjeldahl-method consumed 11,6 cc. of $N./_{10}$ sulphuric acid, corresponding with 7,7 pCt. of nitrogen.

0,2410 gr. consumed 12,8 cc. $N./_{10}$ acid, corresponding with 7,4 pCt. of nitrogen.

Determination of the molecular weight.

											Mol. Weight.
0,0820	gr.	of	echinopsine	in	17,5	gr.	of	benzene	gives an increase of	0,07°	157
0,5063	"	"	"	"	11,9	"	"	alcohol	" " "	0,28°	175
0,5740	"	"	"	"	17,5	"	"	benzene	" " "	0,46°	185
0,3310	"	"	"	"	17,5	"	"	"	" " "	0,70°	177
0,9890	"	"	"	"	17,5	"	"	"	" " "	0,79°	186
0,1990	"	"	"	"	17,5	"	"	"	" " "	0,16°	185
0,5020	"	"	"	"	17,5	"	"	"	" " "	0,43°	174

The elementary composition may be expressed by the formula C_{11} H_9 NO. The analytical figures also agree well with $(C_{11}$ H_{10} NO$)_2$, but this formula must be rejected on account of the results of the determination of the molecular weight.

	Found.						Calculated for C_{11} H_9 NO.
	I.	II.	III.	IV.	V.	VI.	
H.	6,0	6,2	6,0	5,6	—	—	5,3
C.	—	76,9	76,4	76,8	—	—	77,2
N.					7,4	7,7	8,2
O.	—	—	—	—	—	—	

The calculated molecular weight of this formula is 171; the average of the found molecular weight is 177.

Estimation of water in hydrated echinopsine.

Found.				Calculated for C_{11} H_9 NO, aq.
10,3 pCt.	10,0 pCt.	10,0 pCt.	9,3 pCt.	9,5 pCt.

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Analysis of some salts of echinopsine.

Echinopsine hydrochloride. Is a gritty crystalline powder, easily soluble in warm water, and even in the cold more freely soluble than the free base. If a crystal of hydrated Echinopsine is added to a drop of dilute hydrochloric acid, it changes into a white crystalline powder, which disappears on warming. On slow evaporation the salt is deposited in fine, large rhombohedra, on rapid evaporation in microscopic six-sided plates. The hydrochloride is well adapted for physiological experiments; at first it tastes acid, afterwards persistently bitter. It loses hydrochloric acid already at 105°. The air-dried salt, pressed between blotting-paper, retains from 6,9—14,4 pCt. of water (2 mols. of water = 14,8 pCt.), which it soon loses when placed in a dessiccator over sulphuric acid.

Amount of hydrochloric acid (of the anhydrous salt).

1) 0,2080 gr. takes 0,972 cc. N./potash or 0,0352 gr. or 16.9 pct. of H Cl.
2) 0,1367 „ „ 0,631 „ „ „ 0,0232 „ „ 16.9 „ „ „
3) 0,2147 „ „ 1,025 „ „ „ 0,0374 „ „ 17.4 „ „ „

Found.			Calculated for $C_{11} H_9 NO$, H Cl
16,9 pct.	16,9 pct.	17,4 pct.	17,7 pct.

Echinopsine sulphate. Crystallises very beautifully in elongated colourless needles, which dissolve slowly in cold but easily in warm water.

The sulphates prepared by me contained respectively 26,0 pct. (8 mols. = 24,6 pct) and 8,2 pct. (2 mols. = 7,6 pct.) of water.

Amount of sulphuric acid (calculated on the anhydrous sulphate).

1) 0,1777 gr. of anhydr. sulph. takes 0,840 cc. of N. potash or 0,0412 gr. or 23,2 pct. of $H_2 SO_4$
2) 0,1139 „ „ sulph. + 2 aq. „ 0,490 „ „ „ „ 0,0240 „ „ 22,9 „ „ „

Found		Calculated for $(C_{11} H_9 NO)_2$, $H_2 SO_4$
23,2 pct.	22,9 pct.	22,3 pct.

Echinopsine nitrate. Is also crystalline and not easily soluble in cold, easily soluble in warm water.

Amount of nitric acid (of the anhydrous salt).

1) 0,1462 gr. takes 0,640 cc. N.potash or 0,0403 gr. or 27,5 pCt. of HNO_3
2) 0,0521 „ „ 0,230 „ „ „ 0,0145 „ „ 27,8 „ „ „

Found		Calculated for $C_{11} H_9 NO$, HNO_3
27,5 pCt.	27,8 pCt.	26,9 pCt.

Echinopsine oxalate. A beautifully crystallised salt which, when air-dried, contained 18,1 pCt. of water (4 mols. = 14,3 pCt.).

Amount of oxalic acid (in the anhydrous salt).

0,1777 gr. takes 0,830 cc. N.potash or 0,0373 gr. or 20,9 pCt. of $C_2 O_4 H_2$

Found	Calculated for $(C_{11} H_9 NO)_2$, $C_2 O_4 H_2$
20,9 pCt.	20,8 pCt.

Echinopsine picrate. A yellow crystalline salt very slightly soluble in water, of varying composition and melting at about 215°, decomposing hereby. The picric acid, present in the alkaloidal salt and

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obtained by shaking with petroleumether after decomposition with sulphuric acid, amounted to 81,1 pCt.

On combustion 0,1040 gr. of the same picrate gave 0,0380 gr. of H_2O and 0,1598 gr. of CO_2.

	Found	Calculated
C.	41,9 pCt.	40,0 pCt.
H.	4,0 „	3,6 „

Echinopsine mercuric chloride. Is beautifully crystalline and melts exactly at 204°. It dissolves easily in boiling water, but requires 120 parts of water at 15°.

Echinopsine mercuric iodide. The precipitate caused in a solution of echinopsine containing a slight excess of hydrochloric acid by Mayer's reagent is a yellowish-white, sticky, substance, which becomes coarsely crystalline when recrystallised from alcohol of 50 pCt. and melts at 178°. 0,150 gram of echinopsine yielded 0,455 gram of this bi-iodide, dried at 100°.

Found	Calculated for $(C_{11}H_9NO, HJ)_2 + HgJ_2$.
33,0 pCt. of alkaloid.	32,6 pCt.

Echinopsine acetate. Is also crystalline and readily soluble, even in cold water, to a bitter fluid; the salt is very unstable and loses its acetic acid completely at 100°.

Iodo-echinopsine. The crystalline precipitate produced by a solution of iodine in a liquid containing echinopsine differs in colour and composition according to the concentration and excess of the iodine employed; it also readily loses some of the iodine. It is somewhat soluble in boiling water and separates on cooling with a light-chocolate colour. When carefully dried, washed with carbon disulphide and recrystallised from alcohol, it forms a coffee-coloured crystalline powder, which melts at about 135°, but gets already sticky before that temperature is reached.

As regards the nature of Echinopsine, the following should be observed. It cannot escape notice that this substance behaves chemically more like an amide than an amine, namely like a cyclical amide, while the physiological action is strychnine-like similar to piperidone, pyrrolidone etc. To this may be added that the colouration with ferric chloride and the empirical composition also seem to point to a substance as phenylpyridone. I made some reduction and oxidation experiments [1]) to learn the structure of Echinopsine,

[1]) *Reduction of echinopsine.* Heated in a combustion tube with zinc dust in a slow current of hydrogen, echinopsine yields a distillate consisting of a yellowish-brown oily liquid having the odour of pyridine; it is heavier than water and insoluble therein but is readily dissolved on adding hydrochloric acid. This solution was

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but the greater portion of my material had already been exhausted by the general study of this new substance. I can only say, that Echinopsine, although not identical with the phenylpyridone described in the *Berl. Ber.* XXIX, 1697 is probably related to the same.

The analysis of *Echinops* is not completed with the investigation of crystalline Echinopsine.

There are, namely, indications that other special substances occur in this material. In the first place it must be observed that the crystalline Echinopsine possesses only a part of the bitterness of the raw material; a decoction of the fruits is still bitter in the proportion of 1 : 3000—4000, Echinopsine hardly any more at 1 : 30.000; there must, therefore, exist some other active components which cause or increase this bitterness.

The precipitate from Mayer's reagent in the acidulated aqueous solution of alcoholic extract of echinops is much more considerable than can be accounted for by the quantity of echinopsine which might be prepared from it, and it even amounts to 0,2 gram for 1 gram of seed, being of a different nature than the precipitate obtained by Mayers reagent in an acidulated watery solution of pure Echinopsine; it has for instance a much higher melting-point.

I have devoted no small amount of labour to the study of these other constituents, but for the present I can only offer the Echinopsine in a pure condition and venture some information about the accompanying alkaloids, without wishing to pretend that the following alone account for the missing echinops-alkaloid-complex.

It has already been mentioned that the purified total-alkaloid, when repeatedly recrystallised from benzene, gradually acquires a higher melting-point. There is present a crystalline accompanying alkaloid

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repeatedly washed with ether, the base was liberated with aqueous caustic potash, distilled in a current of steam and removed from the milky distillate by means of ether. It was thus obtained as a colourless liquid of the same main properties as the crude distillate, namely heavier than water and insoluble in the same. With hydrochloric acid it forms a compound soluble in water of a burning taste giving crystalline precipitates with picric acid (yellowish-white), platinum and gold chlorides (first yellow, afterwards pale-red) which all melt and decompose at 200°; also a compound with mercuric chloride consisting of velvet-like white needles melting at 159°. These data do not admit of any identification with one of the known phenylpyridines.

Oxidation of echinopsine. Echinopsine was oxidised in the cold with 6 times its weight of a neutral 4 pCt. solution of potassium permanganate, the filtrate was treated with carbon dioxide, evaporated to dryness and the residue extracted with alcohol containing hydrochloric acid; this left undissolved a nitrogenous, hygroscopic substance soluble in water but insoluble in ether. It begins to melt at about 120° and yields on stronger heating an oily distillate having the odour of pyridine and diphenylamine.

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(*β-Echinopsine*), which behaves in most respects like Echinopsine, but passes readily from the acid solution into chloroform, gives no colour reaction with ferric chloride, contains less carbon than Echinopsine, is a still more weak base and melts at 135°.

Mention has also already been made of the substance soluble in water, alcohol, amyl alcohol and benzene, which causes the green fluorescence of the solutions of the crude alkaloid, *Echinops-fluorescine*. The benzene motherliquor obtained in the preparation of Echinopsine, leaves on evaporation a dark brown mass; this was dissolved in dilute acetic acid, washed with petroleumether and ethylether and then again shaken out with chloroform; the fluorescine passes from the acid, but more readily from the alkaline solution, into that solvent. It was dissolved in acidulated water and precipitated with picric acid. The picrate, after being washed with water and dried between blotting paper, formed a sulphur-yellow crystalline cake melting at 210°. This picrate was decomposed with an aqueous caustic potash of 10 pCt. and the base thus liberated was taken up with chloroform; it seemed to be admixed with much Echinopsine. After this had crystallised out, the fluorescine remained as a brown resinous substance of alkaloidal nature, melting at 105°, not bitter, and with an extraordinarily large fluorescing power. The green fluorescence of the light brown solution is not changed by alkalies; addition of acids renders it colourless but on exposure to the air it soon regains its colour and fluorescence. The yield of fluorescine is small, the fruits of *E. exaltatus* containing a larger quantity of it than any other species, examined yet. To judge from the picrate precipitate, the purified material of *E. Ritro* contains about 0,10 pCt.

There is also in the motherliquor a non-fluorescent amorphous alkaloidal constituent, *Echinopseïne*, present. It is a brown mass decomposing on the waterbath and turning cherry-red thereby; this change of colour is also caused by alkalis. From an acid, but more readily from an alkaline solution, it passes into chloroform. The solution in very dilute sulphuric acid is bitter-adstringent, has a flavour of benzylaldehyde and gives with picric acid an abundant yellowish-green precipitate, also melting above 200°, decomposing thereby. This picrate was also decomposed by aqueous caustic potash and the base dissolved in chloroform; the chloroform residu, which was cherry-red, still contained much Echinopsine; the Echinopseïne being obtainable only as a resinous mass, melting at 125°; I therefore, had to give up further research in this direction.

Both Echinopseïne and Echinops-fluorescine obstinately adhere to

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Echinopsine, causing this to exhibit for a long time a green fluorescence and to turn occasionally pink, when moistened with distilled water. This colourreaction is caused by a trace of alkali, presents in the distilled water, from the glass vessel.

Finally a few words on *Echinops oil*, which is met with when extracting the alkaloid. When quantitatively estimating the oil by extraction with ether, 27,5 pCt. was found in the seed of *E. Ritro*. It is a pale yellow sweet thick oil, of 0,930 sp. gr. at 15°, slowly drying. It has the striking property to dissolve on warming in an equal volume of absolute alcohol; on cooling an emulsion is formed and then the oil separates almost completely; at 15° the oil requires about 25 parts of alcohol for solution. Methylalcohol does not possess this remarkable property [1]). The oil is soluble in all proportions in kerosene, ether, carbon disulphide and benzene, also in an equal volume of warm glacial acetic acid. The saponification number of the oil is 194°, the melting point of the solid fatty acids 41° and the solidifying point 39°.

M. GRESHOFF

Laboratory, Colonial Museum, Haarlem.

ADDENDUM I.

On the physiological action of echinopsine.

By Professor Dr. R. KOBERT.

In October 1899, I received from Dr. M. GRESHOFF of Haarlem half a gram of crystallised Echinopsine hydrochloride.

With this small quantity only 3 experiments could be made with frogs and 2 with guinea-pigs.

These, however, sufficed to establish the following facts:

1. Echinopsine hydrochloride is a poison for cold-blooded and warm-blooded animals (frogs and guinea-pigs).

2. With both classes of animals the actions are similar and consist of an irritation of the motor-centres of the nervous system.

3. Both brain and spinal chord are taking part in this irritation. The irritation of the brain is only noticed in the case of warm-blooded animals and then shows itself as trismus and most violent spasmodic contraction of the masseteres. The irritation of

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[1]) Other fatty oils from the seeds of the Compositae are also more soluble in boiling alcohol than is usually the case, but not to such an extent as Echinops oil. Madia oil for instance, requires 6 parts of boiling and 30 parts of cold alcohol.

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the spinal chord which, in the case of the frog, is not stopped by severing the brain, is apparent from the convulsion of all the four extremities. In the case of warm-blooded animals these may appear as klonus and tonus occasionally even as opisthotonus.

4. When a very large dose is administred to a frog, the irritation instantly passes into paralysis, whilst with a smaller dose the irritation symptoms may continue for 4—5 hours.

5. When a dose is administred to cold-blooded animals in sufficient quantity to cause irritation, it will be noticed that before the first convulsions set in and during the intervals, there exists a state of torpor, dotage and reflex-debility.

6. In the experiments on frogs the heart is decidedly weakened and such by doses which do not yet paralyse the spinal chord.

7. The complete action of echinopsine reminds of that of a mixture of strychnine and brucine but is not identical with the same, as the ophisthotonus and the reflex-irritation are not so marked as with minimal doses of strychnine and also because the heart is more affected than is the case with strychnine.

8. Doses: A subcutane dose of 0,02 gr. does not affect esculentae of ordinary size (winter frogs); 0,05 gr. causes an irrition lasting, with intervals, for several hours; 0,08 gr. paralyses the nervous system without previous irritation and also paralyses the heart at the same time.

A dose of 0,10 gr. has no visible effect on a guinea-pig weighing 325 gr., but 0,25 gr. kills the animal after suffering violent spasms for several hours.

9. Antidotes for echinopsine are to be looked for among those narcotics which do not weaken the heart.

10. It is not probable that anatomical changes occur in echinopsine poisoning cases, but I will pay attention to this matter when making experiments with the fresh material recently received from Haarlem.

Institute for pharmacology and physiological
chemistry, University, Rostock.

ADDENDUM II.

On the localisation of echinopsine.

By Professor Dr. E. VERSCHAFFELT.

The research on the microchemical localisation of echinopsine in the tissues will form the subject of an elaborate paper in which

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it will also be attempted to trace the relation between this localisation and the physiological signification of the alkaloid. Provisionally, attention will only be called to a few particulars respecting the distribution of echinopsine in the fruit of *Echinops Ritro*. For this purpose the method originally proposed by ERRERA was employed [1]), which is based on the precipitation of the alkaloid in the cells by means of iodine dissolved in potassium iodide or alcohol. With some plants mistakes may be made when using this method on account of the presence of other substances which also give precipitates with iodine such as amines, glucosides, albuminoids; but when dealing with *Echinops* no fear need be entertained as the iodo-echinopsine precipitate is not like the others [2]) in the form of a minute granular brownish-red precipitate but in large exceedingly characteristic crystals. The crystals formed in the tissues will be found under the microscope to be similar in appearance to the iodo-compound of pure echinopsine. As solutions of iodine were so eminently satisfactory it was not thought necessary to use other reagents on an extensive scale. The manner these behave towards the alkaloid in the tissues will be mentioned later on.

The scales of the involucrum which surround the ripe fruit in a dry condition, are free from alkaloid just like the dry fruit walls and their toothed hairs. The cells of the embryo, on the contrary, are mostly rich in alkaloid. This fleshy straight embryo practically occupies the space of the coalesced fruit-wall and seed-coat as far as the latter is developed. The embryo is surrounded with a double layer of thick-walled cells which like the cells of the embryo itself are filled with reserve material.

The morphological nature of this membrane which easily detaches either way from the embryo, as well as from the fruit-wall, cannot be explained with certainty without watching the course of development. It may be a rudimentary endosperm, also a seed integument. The cells of the embryo contain fatty oil and albuminoids as reserve materials. The fatty oil may be rendered visible in the ordinary way by killing the cells, for instance, by heating or by means of an acid which causes the oil to be liberated and collect in large drops. The cells are closely filled with aleuron-granules, which are present in such large numbers that they are only separated from each other by a network

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[1]) ERRERA, MAISTRIAU et CLAUSTRIAU. *Ann. Soc. Belge de Microsc.* 12, 1889. ERRERA *ibid.* 13, Mémoires.

[2]) Compare the researches of DE WÈVRE, DE WILDEMAN, ANEMA, MOLLE, LOTSY, BARTH and others.

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of thin plates consisting of amorphous oil-containing protoplasm and often flatten one another (see Fig.). These aleuron-granules are small, their diameter being at the most one third of the size of those of *Ricinus* and *Linum*, but they are fairly equal in size. Their further structure may be silently passed over.

The cells of the already mentioned double layer present around the embryo also contain granules of an albuminous nature but these are much smaller than the aleuron-granules of the embryo.

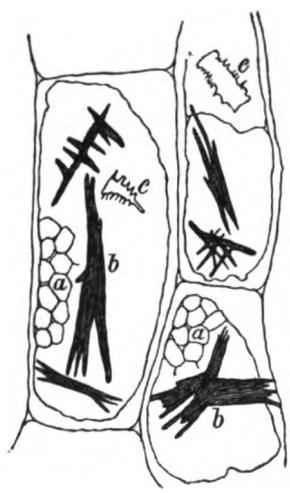

Fig.

a. borders of the aleuron-granules.

b. most numerous needle-shaped aggregations of the iodo-echinopsine compound.

c. less numerous brown plates.

Annexed figure gives a representation of a group of cells from the cotyledons of *Echinops Ritro* after treating a section with glycerol mixed with tincture of iodine until the mixture assumed a mahogany-brown colour. I have made frequent use of this mixture as well as of iodine dissolved in potassium iodide. After the sections had stayed for a while in the mixture, they were preserved and mounted in pure glycerol.

The figure does not, however, show what is seen the moment the objects are treated with the reagent, then large crystals are not formed at once. In the beginning a minute brownish-red granular precipitate is obtained which, however, unites after a few minutes to the larger aggregations of dark coloured needles, as shown. It is interesting to watch under the microscope the first formation of the precipitate; it then appears to form in the aleuron-granules which instantly turn brownish-red and show afterwards inside their mass darker and larger crystals. The amorphous protoplasm between the aleuron-granules turns at once pale yellow and remains so. Echinopsine occurs, therefore, only in the aleuron-granules and was in consequence formed within the *vacuolae* of the unripe seed, which is as might be expected.

The crystals which are visible in the cells after some time belong to two very plainly different forms. The more numerous are dark coloured manifoldly-grouped needles *b*. These agree, as regards appearance, very well with the precipitate caused in a solution of pure echinopsine of which Dr. GRESHOFF was kind enough to present me with a certain quantity. Between these needles are noticed a smaller number of light brown, more plate-like crystals of a peculiar feathery appearance *c*, which I have not been able to observe in the iodine-

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precipitate of the pure alkaloid, at least under the conditions in which I worked, so that I feel inclined to suspect the presence of the iodo-compound of an accompanying alkaloid. The double peripheric layer of the seed contains alkaloid. In the cotyledons, a beginning of differentiation is observable in palisade and spongy parenchyma, a phenomenon occurring in different plants the cotyledons of which afterwards turn green and assimilate (for instance, *Brassica*, *Linum*). There is, apparently, no difference in the amount of alkaloid contained in the tissues. The epidermis of the cotyledons also contains much alkaloid. The procambium bundles which traverse the seed lobes are, on the other hand, perfectly free from alkaloid and the same is true of those of the root. The bark of the latter is quite as rich in echinopsine as the tissue of the cotyledons.

The centre of the root which is surrounded by the procambium bundles is poor in alkaloid, so that here, a cylinder poor in alkaloid is separated from the bark rich in alkaloid by a layer free from alkaloid.

This want of alkaloid in the procambium of the embryo is interesting because, as will be more fully demonstrated later on, tolerably much alkaloid is actually found in the bast (phloem) in the further course of the development.

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Physics. — "*On the relation between Radiation and Molecular Attraction*". By J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

At the end of a paper in the Proceedings of the Royal Acad. of Sciences of March 1900 I expressed my intention of investigating whether the ponderomotoric action of radiation could give an explanation of molecular attraction. The course which I would take, was the solution of the equations of motion of a number of vibrators which act on each other and are subjected to no other forces. If we could solve these equations, and if this action proved sufficient to explain the molecular attraction, we might be able to deduce from this whether the quantity a of the equation of state is a function of the temperature, and if so, what function, and whether the attraction is really proportional to the square of the density, or if it is so only by approximation.

I have however, not succeeded in finding the function solution of this problem, not even for the case that there are only two

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vibrators. Nor is the general solution, to be used. The action of the molecular force is only felt if the distance of the molecules is very small. Then $\frac{r}{V}$ or $t'-t$ is very small and we should have to take into account a great many terms.

The following considerations may however serve for a preliminary investigation as to whether the order of the quantity of the forces of radiation is the same as that of the molecular forces, or whether they are so small that we are forced to assume that there acts besides the forces of radiation, another kind of force between the molecules.

For this purpose we examine how much smaller the quantity of energy is, which a set of vibrators has, when they are influenced by one another, than the sum of the energy which every vibrator would have separately, if it were alone in space with its own amplitude. The difference of these two quantities of energy may be considered as the energy which the vibrators would lose if they were brought from an infinite distance to the places they now occupy, provided care be taken, that they had the same amplitude during the whole process (i. e. that the process was carried out isothermically).

An exact solution of this problem would be very intricate and the energy of the field would certainly have to be taken into consideration. I shall, however, assume that the energy to be found is by approximation represented by:

$$\tfrac{1}{2} \Sigma 4\pi V^2 (f a_x + g a_y + h a_z).$$

This comes to the same thing as if we put the moment of a vibrator o at a given moment and then seek the difference of the following two quantities of energy:

1st The energy necessary for giving the moment a to the molecule when it is not subjected to any action of other molecules.

2nd The energy necessary for giving the moment a to the molecule, when it is in a region, where the electrical displacement has the components f, g, h.

If we take the sum of these quantities of energy for all molecules, we have taken both the energy which molecule I has with respect to molecule II and that which molecule II has with respect to molecule I. We have therefore to divide the result by 2.

If the quantities a_x and f were independent of each other, $f a_x$ added for all the molecules, would yield o. In consequence, however, of the partial regulation of the vibrations of the molecules with respect to the electric forces, f and a_x will not be independent.

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(Compare "Entropy of Radiation II," Proc. Roy. Acad., Febr. 1900). The same holds of course also good for $g\,a_y$ and $h\,a_z$.

I shall assume that every molecule on an average has absorbed the amplitude $\sigma\,b$ from the field. If we knew σ as function of the temperature and of the density for every substance we had a complete solution of the problem. We do not know σ however, and can only compute how great σ must be in order that the forces of radiation account for molecular attraction. We must find a fraction and we may expect that the fraction will not be *very* small.

For f I shall take the value as it is calculated in "Entropy of Radiation I," (Proc. Roy. Acad., Dec. 1899). In doing so we are guilty of the inconsistency of taking a value for f, calculated on the supposition, that the motion is perfectly irregular, while the energy which we are seeking, is the very consequence of the partial regulation. We cannot, however, calculate another value for f, if the way of regulation is not known and the mistake which we make in doing so, is probably slight.

The mean value of $g\,a_y$ and $h\,a_z$ being equal to that of $f\,a_x$, we may write for the energy:

$$E = \frac{3}{2}\,\Sigma\,4\,\pi\,V^2 f\,a_x$$

and we need only take those terms of a_x which are caused by the forces of the field; so:

$$E = 6\,\pi\,V^2\,\sigma\,\Sigma\left(f_1 \cos\frac{2\,\pi\,t}{T} + f_2 \sin\frac{2\,\pi\,t}{T}\right) \times$$

$$\left(b_{x1}\cos\frac{2\,\pi\,t}{T} + b_{x2}\sin\frac{2\,\pi\,t}{T}\right)$$

where

$$b_{x1} = p\,f_1 + q\,f_2 \qquad b_{x2} = -\,q\,f_1 + p\,f_2$$

$$p = -\,4\,\pi\,\frac{V^2 e^2}{m}\,\frac{\dfrac{4\,\pi^2}{T^2} - \dfrac{f}{m}}{\left(\dfrac{4\,\pi^2}{T^2} - \dfrac{f}{m}\right)^2 + \left(\dfrac{2}{3}\right)^2 \dfrac{e^4}{m^2}\,\dfrac{1}{V^2}\left(\dfrac{2\,\pi}{T}\right)^6}\,,^{1})$$

$$q = -\,4\,\pi\,\frac{V^2 e^2}{m}\,\frac{\dfrac{2}{3}\,\dfrac{e^2}{m}\,\dfrac{1}{V}\left(\dfrac{2\,\pi}{T}\right)^3}{\left(\dfrac{4\,\pi^2}{T^2} - \dfrac{f}{m}\right)^2 + \left(\dfrac{2}{3}\right)^2 \dfrac{e^4}{m^2}\,\dfrac{1}{V^2}\left(\dfrac{2\,\pi}{T}\right)^6}$$

[1]) See note at the end of this paper.

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On an average the terms containing $\sin \frac{2\pi t}{T} \cos \frac{2\pi t}{T}$ will become zero and also those containing the product $f_1 f_2$. As the mean of both $\sin^2 \frac{2\pi t}{T}$ and $\cos^2 \frac{2\pi t}{T}$ is $\frac{1}{2}$, and the mean of f_1^2 equal to that of f_2^2, we find:

$$E = 6\pi V^2 \sigma p \Sigma f_1^2$$

For Σf_1^2 we may write $\frac{1}{3} n \varepsilon^2$, in which n represents the number of molecules per unity of volume and ε the quantity, defined at pag. 322 (Proc. Roy. Acad., Dec. 1899). For ε we may, however, not take the approximated value calculated there, which holds only for points at some distance from the source.

Let us represent a volume-element by $r^2 dr \sin\theta d\theta d\varphi$ and let us call the shortest distance, to which two molecules can approach ρ, then:

$$\varepsilon^2 = 2 n \overline{a_{x_1}^2} \frac{1}{(4\pi)^3} \int_\rho^\infty \int_0^\pi \int_0^{2\pi} r^2 dr \sin\theta d\theta d\varphi \, e^{-2\mu r}$$

$$\left\{ \left(\frac{y^2+z^2}{r^3} \frac{4\pi^2}{\lambda^2} + \frac{3x^2}{r^5} - \frac{1}{r^3} \right)^2 + \left(\frac{3x^2}{r^4} - \frac{1}{r^2} \right)^2 \frac{4\pi^2}{\lambda^2} + \right.$$

$$\left. + \frac{x}{r^6} (y^2+z^2) \left[\left(\frac{4\pi^2}{\lambda^2} - \frac{3}{r^2} \right)^2 + \frac{9}{r^2} \frac{4\pi^2}{\lambda^2} \right] \right\}$$

$$\varepsilon^2 = 2 n \overline{a_{x_1}^2} \frac{1}{16\pi^2} \int_\rho^\infty \int_0^\pi \int_0^{2\pi} r^2 dr \sin\theta d\theta d\varphi \, . \, e^{-2\mu r}$$

$$\left[\left(\frac{4\pi^2}{\lambda^2} \right)^2 \frac{1}{r^2} \sin^2\theta + \frac{4\pi^2}{\lambda^2} \frac{1}{r^4} (5\cos^2\theta - 1) + \frac{1}{r^6} (3\cos^2\theta + 1) \right].$$

If we take into consideration that:

$$\int_0^\pi \sin^3\theta d\theta = \frac{4}{3} \quad \text{and} \quad \int_0^\pi \sin\theta \cos^2\theta d\theta = \frac{2}{3}$$

this becomes:

$$\varepsilon^2 = 2 n \overline{a_{x_1}^2} \frac{1}{8\pi} \int_\rho^\infty \left[\left(\frac{4\pi^2}{\lambda^2} \right)^2 \cdot \frac{4}{3} + \frac{4\pi^2}{\lambda^2} \cdot \frac{1}{r^2} \cdot \frac{4}{3} + \frac{4}{r^4} \right] e^{-2\mu r} dr \, .$$

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The first term may be at once integrated and furnishes:

$$\frac{1}{2\mu}\left(\frac{4\pi^2}{\lambda^2}\right)^2 \frac{4}{3} e^{-2\mu\rho}.$$

The two other terms cannot be integrated; if however we omit the factor $e^{-2\mu r}$, the last term becomes predominant, viz $12\frac{1}{\varrho^3}$. The terms with small r appear to have most influence, even if $e^{-2\mu r}$ is omitted. This is a fortiori true if the factor $e^{-2\mu r}$ is preserved. For terms with very small r the factor $e^{-2\mu r}$ is nearly 1, so that $12\frac{1}{\varrho^3}$ is really an approximated value of the integral of the third term. Further $\frac{1}{\varrho^3}$ is great compared with $\frac{1}{2\mu}\left(\frac{4\pi^2}{\lambda^2}\right)^2$, so that we may write by approximation:

$$\varepsilon^2 = 3n\frac{1}{\pi}\overline{a^2_{\varkappa 1}}\,\frac{1}{\varrho^3}.$$

In order to determine the quantity $\overline{a^2_{\varkappa 1}}$ we take into consideration that for one vibration the quantity of energy, emitted per second is equal to $\frac{2}{T}\frac{8}{3}V^2\frac{\pi^4}{\lambda^3}a^2$. As $\overline{a^2_{\varkappa 1}} = \frac{1}{6}a^2$, we find:

$$\varepsilon^2 = \frac{3}{32}\frac{1}{\pi^5}n\cdot\frac{\lambda^4}{V^3}I\cdot\frac{1}{\varrho^8}$$

I represents the mean quantity of energy emitted by a molecule. E. WIEDEMANN[1]) calculates that 1 molecule platinum at a temp. of 1000° emits $3{,}3.10^{-16}$ Gr. cal. $= 1{,}4.10^{-8}$ erg. per second.

If we accept the law of STEPHAN, we find for I at about 0° the value:

$$\frac{1{,}4}{5^4}\,10^{-8}\text{ erg.} = 2{,}2\;10^{-11}.$$

For the quantity of energy sought we find therefore:

$$E = \frac{9}{32}\frac{1}{\pi^4}n^2\frac{\lambda^4}{V}\frac{1}{\varrho^3}pI\sigma.$$

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[1]) Wied. Ann. XXXVII, 2, Bl. 203.

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We shall use the following approximated values as given:

$$n = 5.10^{19} \qquad \frac{e}{m} = 10^7 \text{ [1]}$$

$$V = 3.10^{10} \qquad \frac{e^2}{m} = 2{,}5.10^{-13} \text{ [1]}$$

$$\varrho = 3.10^{-8}$$

Taking these values into account we can give p a simpler form. To that purpose we determine k from the equation:

$$2k + \frac{e^2}{m}\frac{1}{V}\left(2k^2 - \frac{4\pi^2}{T^2}\right) = 0 \text{ [2]}$$

We have to use the positive root of this equation, which has a value of about 10^7. Now we see that $2k^2$ is small compared with $\frac{4\pi^2}{T^2}$ and may be neglected, so that we may write approximatively

$$k = \tfrac{1}{2}\frac{e^2}{m}\frac{1}{V}\frac{4\pi^2}{T^2}.$$

Let us substitute this in the equation:

$$\frac{4\pi^2}{T^2} - \frac{f}{m} = k^2 + \frac{2}{3}\frac{e^2}{m}\frac{1}{V}\left(k^3 - 3k\frac{4\pi^2}{T^2}\right) \text{ [2]}.$$

The term with k^3 may be neglected, and we find:

$$\frac{4\pi^2}{T^2} - \frac{f}{m} = -3k^2 = -\frac{3}{4}\left(\frac{e^2}{mV}\right)^2\left(\frac{4\pi^2}{T^2}\right)^2$$

This quantity is of the order 10^{14}. The square of it occurs in the denominator of p and is of the order 10^{28}. This term may therefore be neglected, as the other term of the denominator $\left[\frac{e^2}{Vm}\left(\frac{2\pi}{T}\right)^3\right]^2$ is of the order 10^{33}. So we find for p:

$$p = 4\pi\frac{V^2e^2}{m}\frac{\frac{3}{4}\left(\frac{e^2}{mV}\right)^2\left(\frac{4\pi^2}{T^2}\right)^2}{\left(\frac{2}{3}\right)^2\left(\frac{e^2}{mV}\right)^2\left(\frac{4\pi^2}{T^2}\right)^3}$$

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[1] LORENTZ, Versl. Kon. Akad. v. Wetensch., Maart 1898.
[2] Proc. Royal Acad. of Sc. Amsterdam, Febr. 1900, p. 417.

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or

$$p = \frac{27}{16}\frac{1}{\pi}\frac{e^2}{m}\lambda^2 .$$

If we substitute this value for p in E, we find:

$$E = \frac{243}{512}\frac{1}{\pi^5} n^2 \frac{\lambda^6}{V}\frac{e^2}{m}\frac{1}{\varrho^3} I\sigma .$$

So we see that E depends in a high degree on λ, and that the value which we find, is quite determined by the value for λ which we assume. Now the quantity I is determined for a continuous spectrum, and it is not at once to be seen what value for λ we have to take. I shall therefore have to confine myself to calculate, what value λ must have, to make E equal to the energy of the molecular attraction. σ is however also unknown and in order to calculate λ, we have to assume a value for σ. If we put $\sigma = 1$, we know that we take a too great value for σ. The value of λ, which we calculate from it, is therefore the minimum-value which λ must have in order to make E equal to the energy of the molecular attraction.

The energy of the molecular force, is, as we know, represented by $\frac{a}{v}$. For 1 c.c.M. air under normal circumstances this is 2700 erg. For I we have however taken the quantity of energy emitted by one molecule platinum. Therefore we have to take also the quantity $\frac{a}{v}$ for platinum. As substances with great molecular weight have also a great value for a, we shall take a for platinum ten times as great as it is for air, and put therefore:

$$\frac{a}{v} = 27 . 10^3 .$$

That platinum under these circumstances forms a phasis of little stability or perhaps even an instable phasis, is of no consequence.

If we replace E by this value of $\frac{a}{v}$ and further all quantities by their numerical values, we get:

$$27 . 10^3 = \frac{243}{512}\frac{1}{\pi^5}\, 25 . 10^{38}\, \frac{\lambda^6}{3 . 10^{10}}\, \frac{2{,}5 . 10^{-13}}{27 . 10^{-24}}\, 2{,}2 . 10^{-11}$$

or

$$\lambda^6 = \pi^6\, 10^{-24}\, \frac{9 . 512}{137{,}5 . 10 . \pi} .$$

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So we find by approximation:

$$\lambda = 3{,}16 \,.\, 10^{-4} \,.$$

At 0° the wave-length of radiation emitted in a sensible quantity is certainly greater than 10^{-4}, while the greatest wave-lengths measured amount to $\pm\ 22.10^{-4}$. It is therefore no unsatisfactory result that we have to take for λ as minimum $3{,}16 \,.\, 10^{-4}$.

Though the numerical result may not have much value on account of the great uncertainty of the numbers used, yet it pleads rather in favour of the supposition that the cause of the molecular attraction must be looked for in radiation, than against it. The more so, as this supposition is supported by its simplicity. It is true that an accurate calculation of the molecular attraction from the forces of radiation would be pretty intricate, but we cannot doubt of the existence of the forces of radiation and the question is only: "are they the only forces, or does there exist another kind of force acting between the molecules and giving an explanation of the molecular attraction?" And certainly the assumption of the first alternative is simpler than that of the second. In the meantime it will have to appear from later investigations whether this supposition will be able to explain the action of the molecular forces more in particulars.

Note. The values for p and q used here are not quite the same as those which I found for them on pag. 417 Proc. Roy. Acad., Febr. 1900.

Two mistakes occur namely in the values given there. First the two quantities must have the opposite sign. Secondly Prof. LORENTZ has pointed out to me that the formula, from which I start, and which is borrowed from formula 111 of his treatise in the Arch. Néerl. XXV, 5, is not quite correct. The two terms of 111 have both to be multiplied with $^2/_3$.

To demonstrate this, we continue the series of calculations on pag. 486, which is there without good reason stopped at $\dot{x}$, for two terms more, and replace the quantity occurring there:

$$x - \frac{r}{V}\dot{x}$$

by

$$x - \frac{r}{V}\dot{x} + \frac{r^2}{2\,V^2}\ddot{x} - \frac{r^3}{6\,V^3}\dddot{x}$$

For χ_1 we get then the following terms in addition to those which LORENTZ took into account:

$$-\frac{1}{8\,\pi\,V^4}\ddot{x}\int \varrho_0\, r\, d\tau' + \frac{1}{24\,\pi\,V^5}\dddot{x}\int \varrho\, r^2\, d\tau'.$$

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If we neglect the terms with $\frac{d^4x}{dt^4}$ and $\frac{d^5x}{dt^5}$, as they are of the order $\left(\frac{r}{TV}\right)$ with respect to $\ddot{x}$ and $\dddot{x}$ and if we notice that integrals like $\int \rho_0 \frac{xy}{r^5} d\tau'$ are zero, because of the symmetry, these terms of χ_1 contribute only the following terms for f:

$$\frac{1}{8\pi V^2} \ddot{x} \frac{\partial^2}{\partial x^2} \int \varrho_0 r \, d\tau' - \frac{1}{24\pi V^3} \dddot{x} \frac{\partial^2}{\partial x^2} \int \varrho_0 r^2 \, d\tau' .$$

Now:

$$\frac{\partial^2}{\partial x^2} \int \varrho_0 r \, d\tau' = \int \varrho_0 \frac{\partial^2 r}{\partial x^2} d\tau' = \int \varrho_0 \left\{ \frac{1}{r} - \frac{(x-x')^2}{r^3} \right\} d\tau'$$

and

$$\frac{\partial^2}{\partial x^2} \int \varrho_0 r^2 \, d\tau' = \int \varrho_0 \frac{\partial^2 r^2}{\partial x^2} d\tau' = 2 \int \varrho_0 \, d\tau' = 2e .$$

The two new parts of f are together:

$$\frac{1}{8\pi V^2} \ddot{x} \int \varrho_0 \left\{ \frac{1}{r} - \frac{(x-x')^2}{r^3} \right\} d\tau' - \frac{e}{12\pi V^3} \dddot{x} .$$

We have to multiply this with $4\pi V^2 \rho_0 d\tau$, in order to get the corresponding parts of the force acting on the ion in the direction of the x-axis, and then to integrate over the whole ion. This gives:

$$\tfrac{1}{2} \ddot{x} \int \varrho_0 \, d\tau \int \varrho_0 \left\{ \frac{1}{r} - \frac{(x-x')^2}{r^3} \right\} d\tau' - \frac{e^2}{3V} \dddot{x} =$$

$$= \tfrac{1}{2} \ddot{x} \int \varrho_0 \, d\tau \int \frac{\varrho_0}{r} d\tau' - \tfrac{1}{2} \ddot{x} \int \varrho_0 \, d\tau \int \varrho_0 \frac{(x-x')^2}{r^3} d\tau' - \frac{e^2}{3V} \dddot{x}$$

The value of the second term remains the same when we substitute $(y-y')^2$ or $(z-z')^2$ for $(x-x')^2$, and is therefore one third of what we should get, if we substituted r^2 for $(x-x')^2$. The force which is to be added, becomes then:

$$\frac{1}{3} \ddot{x} \int \varrho_0 \, d\tau \int \frac{\varrho_0}{r} d\tau' - \frac{e^2}{3V} \dddot{x} = \frac{4}{3} \pi V^2 \dot{\xi} \int \varrho_0 \omega \, d\tau - \ddot{\xi} \frac{e^2}{3V}$$

and if this is added to the terms of 111, only $^2/_3$ of this last value remains.

Chemistry. — „*Plumieride and its identity with Agoniadine*". by Prof. A. P. N. FRANCHIMONT.

The name Plumieride has been given in 1894 by Dr. BOORSMA of Buitenzorg to a substance which he had isolated from the bark of Plumiera acutifolia. Dr. BOORSMA states i. a. that Plumieride does not

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melt, that it is not a glucoside, that its composition is $C_{30}H_{40}O_{18}+H_2O$ and he concludes that it is a substance quite different from the one prepared in 1870 by Dr. TH. PECKOLT, of Rio de Janeiro, from the bark of Plumiera lancifolia and called by him *Agoniadine*. This substance was analysed and investigated in Jena by Prof. A. GEUTHER who gave it the formula $C_{10}H_{14}O_6$; it melted at 155° and yielded on boiling with dilute sulphuric acid a sugar and a brown, amorphous substance and consequently was a glucoside.

In his review of 1895, it is stated by E. MERCK that he had obtained from the root of Plumiera acutifolia, a substance different from that of BOORSMA, melting at 157—158° with evolution of gas. He gives as its composition $C_{57}H_{72}O_{33} + 2H_2O$ and for its molecular weight 1074—1080, although the given formula requires 1280.

On the occasion of his last visit to Holland, our fellow member Dr. TREUB requested me to re-investigate the plumieride which I agreed to do.

Preliminary experiments made me see at once that plumieride is a polyhydric alcohol, optically active and fairly strong laevogyrate in aqueous solutions; also that it decidedly deserves the name of glucoside and that the sugar obtained in its hydrolysis is birotatory and dextrogyrate and also gives a phenylosazone which is identical with that of glucose, as shown by its melting point and rotatory power. I also noticed that the substance of MERCK behaves in every respect, except in its fusibility, like BOORSMA's plumieride and could show with great probability that the difference is caused by a variation in the amount of water.

When rendered anhydrous, properly purified and crystallised from dry ethylacetate, both appeared to be identical; they do not melt and have the same rotatory power and crystalline form. When recrystallised from water they were again identical, had the same melting point and contained the same amount of water.

Still a difference might have been caused by the fact that BOORSMA had repeatedly boiled his substance with amylalcohol and that it was possible that this is not an inert solvent. I had, therefore, the substance prepared from the bark which had been forwarded to me from Buitenzorg, avoiding the use of amylalcohol and also a high temperature; this preparation after being recrystallised from dry ethylacetate was also identical with the other.

That plumieride yields fairly much glucose on boiling with dilute hydrochloric acid was proved afterwards by isolating the glucose in a pure, crystallised anhydrous state and identifying it by its melting point and rotatory power. At the same time the absence of

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mannose and pentoses was shown. Then if plumieride is boiled with hydrochloric acid of 10—12 pCt. strength, only insignificant traces of furfuraldehyde are formed, while the glucose is decomposed into formic and laevulinic acids, which were both identified, in the company of a humus-like substance which is mixed with the second product of the hydrolysis of plumieride, a brown amorphous substance the weight of which amounts in this case to more than half the weight of the plumieride. On boiling with hydrochloric acid of 5 pCt. strength, glucose may be obtained one-fourth part of the weigth of the used plumieride although laevulinic acid is also formed here, by destruction of a part of the glucose; the weight of the amorphous substance is then about one-half of that of the plumieride. On boiling with hydrochloric acid of half a pCt. strength, the hydrolysis of plumieride also takes place, although much slower, and a part of the glucose may also be decomposed of which I have convinced myself by actual experiment. The brown substance now certainly weighs less than half the weight of the used plumieride, but still always contains a humus-like decompositionproduct of glucose. It is, therefore, plain that the exact quantity of glucose which plumieride is capable of yielding cannot, apparently, be determined in this manner and that the second product from the plumieride is not to be got in a pure state in this way.

I hope to communicate later on, at the close of the investigation, about this brown substance and the hydrolysis of plumieride by enzymes.

After plumieride had been undoubtedly characterised as a glucoside, it was desirable to study *agoniadine* which is also known as such and also gives a brown amorphous substance on hydrolysis, and to explain the difference between both substances, should a difference exist. The difference in melting point goes for nothing.

As bark from Plumiera lancifolia was not obtainable, I have made use of about 5 grams of agoniadine sent by Dr. PECKOLT. This preparation, which was not pure, gave after being repeatedly crystallised from dry ethylacetate a beautifully crystallised substance perfectly resembling anhydrous plumieride in shape as well as in chemical and physical properties. It was not fusible without decomposition and had the same laevorotatory power etc. Our fellow member Prof. BEHRENS had the kindness to compare microscopically different preparations of plumieride with each other and with those obtained from PECKOLT's agoniadine; on account of the fact that they have the same form, polarisation and index of refraction, he thinks he may safely conclude that they are identical. I, then, do not hesitate

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to declare that the substance, isolated from PECKOLT's agoniadine, is identical with plumieride.

Although it is customary in such cases to retain the name given by the first discoverer, it seems to me that the name „plumieride" is preferable. It reminds of both plants from which it is obtained and by its termination it is more suited for a glucoside. I, therefore, obliterate the name „agoniadine", which on account of its termination reminds more of an alkaloïd, from the chemical literature and in future will call *plumieride* the substance discovered by PECKOLT in 1870 in the bark of Plumiera lancifolia, which substance has afterwards been found by BOORSMA and also by MERCK in the bark of Plumiera acutifolia.

Plumieride is a methyl-ester (a methoxyl containing substance) then it yields methyliodide with hydroiodic acid of a certain concentration. It yields, by the action of dilute alkalis or barytawater at the ordinary temperature, or by water alone at a higher temperature, an acid which I have provisionally called *plumieridic* acid [1]). This does not contain methoxyl but is a glucoside which on boiling with dilute acids yields a brown amorphous substance and a sugar, the osazone of which has the same melting point as that of glucose.

If plumieride is now simply a methyl-ester of plumieridic acid as nearly everything found as yet seems to bear out, the easy decomposition (saponification) by alkalis and even by water and the consequent difficulty to obtain a pure preparation by recrystallisation from water becomes apparent.

I, finally, wish to add that the solution of PECKOLT's preparation in cold water was of a very brown colour and strongly reduced FEHLING's solution; when first extracted with ethylacetate it left a good deal of a brown amorphous substance behind and it was only by repeated crystallisation from ethylacetate, which operation was attended with great loss, that it was obtained pure. The impure fractions contained glucose.

Chemistry. — "*On the crystallised constituent of the essential oil of Kaempferia Galanga L.*" By Dr. P. VAN ROMBURGH.

When the rhizomes of *Kaempferia Galanga L.*, a plant belonging to the family of the Zingiberaceae, which is cultivated on a small scale by the natives in Java for medicinal and culinary use and

[1]) The name plumieric acid has already been given by our deceased fellow member Prof. A. C. OUDEMANS JR. to another acid obtained from the milky juice of Plumiera acutifolia.

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known under the name of "kentjoer" or "tjekoer", are distilled with water, the first fractions contain a small quantity of an essential oil lighter than water. Afterwards an oil heavier than water distils which deposits abundant crystals, whilst towards the end a crystalline substance is almost exclusively obtained. The distillation must be continued for a long time as this substance is but little volatile. The yield and also the relation between the solid and liquid product differ very much with different samples; most likely this depends on the age of the rhizomes, which matter I am now making the subject of practical investigation.

The crystals deposited from the oil may assume very large dimensions; they are very shining and transparent, melt at 50° and may be obtained in a beautiful form by recrystallisation from alcohol. A 20 percent alcoholic solution appeared to be optically inactive.

The elementary analysis gave numbers, which lead to the formula $C_{12} H_{14} O_3$, while the molecular weight, determined in acetone by LANDSBERGER's method, came to 197, 206 being calculated.

On heating with alcoholic potash this substance yielded almost at once a mass of beautiful little crystals of a potassium salt, from which sulphuric acid liberates an acid crystallising in colourless needles. This acid is not easily soluble in water but easily soluble in ether and it may be very satisfactorily recrystallised from dilute methyl alcohol.

The melting point is 169°; at that temperature it melts to an opalescent liquid which does not become transparent till 185°.

The elementary analysis gave results corresponding with the composition $C_{10} H_{10} O_3$.

The original substance differing from this by $C_2 H_4$ must, therefore, be an ethyl-ester. To further prove this, 30 gram of the crystals were saponified with aqueous caustic potash and the resulting alcohol was distilled off. After treatment with dry potassium carbonate and rectification over anhydrous copper sulphate a liquid was obtained which boiled at 78° and showed all the properties of ethyl alcohol.

The potassium and silver salts of the acid were prepared and analysed. The potassium estimation gave 17.7 pCt. of K (theory requiring 17.6), the silver estimation gave 38.06 pCt. Ag., (theory requiring 37.9).

If a solution of the acid in ethyl alcohol is treated with hydrogen chloride, a product is obtained which melts at 50° and is identical with the original ester. The methyl ester prepared in an analogous manner melts at 90°.

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The solution of the acid or its ester in chloroform absorbs two atoms of bromine forming an addition product.

The acid does not show either aldehydic, alcoholic or phenolic properties. Heated with hydriodic acid it yields alkyl iodide. A quantitative estimation according to ZEISEL gave an amount of silver iodide corresponding with 16.85 pCt. of methoxyl, theory requiring 17.4 pCt.

On oxidation with potassium permanganate in neutral solution, the ester gives off an agreeable odour resembling hawthorn, while an acid is also produced which proved to be identical with anisic acid. The oxidation of the acid in an alkaline solution proceeds more quickly; the odour of anisic aldehyde is also noticed here and a good yield of anisic acid is obtained. From this it follows that in regard to the side-chain the group OCH_3 is situated in the para-position and in connection with the additive power the formula is therefore, most probably 1.4 $C_6H_4 \begin{matrix} OCH_3 \\ CH = CH - COOH \end{matrix}$, consequently that of p. methoxycinnamic acid.

The properties do indeed correspond with those recorded of this acid [1]). The only thing which is not mentioned is the peculiar behaviour on melting, so that I thought it necessary to prepare the synthetical acid for comparison purposes.

According to KNOEVENAGEL [2]) it is obtained by condensation of anisic aldehyde with malonic acid under the influence of alcoholic ammonia. The acid prepared by this method also melted at 169° to an opalescent liquid which did not get clear till 185°.

VORLÄNDER [3]) obtained the ethyl ester of p. methoxylcinnamic acid by condensation of anisic aldehyde with ethyl acetate. This I also prepared and found it to be identical with the product obtained from "Kentjoer", whilst the acid obtained from it by saponification again showed the properties mentioned above.

I dare not, as yet, decide what may be the cause of this peculiar behaviour. Perhaps a polymeric body is formed, or else the acid exists in two liquid isomeric modifications [4]). By heating above the melting point, the acid is gradually decomposed with evolution of carbon dioxide, but if the decomposition already exercised some

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[1]) In Beilstein's Handbuch it is erroneously stated that p. methoxycinnamic acid cristallises in yellow needles.

[2]) Berl. Ber. 31 S. 2606.

[3]) Ann. der Chemie. 294, S. 295.

[4]) Compare: RUDOLF SCHENCK, Untersuchungen über die krystallinischen Flüssigkeiten. Zeitschr. f. phys. Chemie XXV, S. 337, XXVII S. 167.

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influence during the determination of the melting point, this would be found lower on repeating the experiment, but this is, however, not the case.

By treating the alcoholic solution of the acid obtained from kentjoer with sodium amalgam p. methoxyphenylpropionic acid is formed, which melts at 102° and has already been described by WILL [1]). The methyl ester of methyl naringeninic acid [2]) prepared by the same chemist, which is identical with the methyl ester of p. methoxycinnamic acid, melts at 90° just like the methyl ester obtained by myself, whilst its bromine-addition product showed the melting point of the methyl ester of dibromomethylparacumaric acid.

There cannot, therefore, be any further doubt that the crystallized substance which forms the chief constituent of the essential oil from *Kaempferia Galanga L.*, is the ethyl ester of p. methoxycinnamic acid, a substance which had not yet been met with in nature and which now goes to increase the comparitively small number of known ethyl esters from the vegetable kingdom.

From the liquid portion of the oil I could separate in addition to the above mentioned ester a small quantity of a terpene boiling at 160°—170° and a bluishgreen liquid boiling at 150° in vacuo (probably a sesquiterpene). There is also present an acid of a lower melting point which I am still investigating.

Pathology. — "*On the durability of the agglutinative substances of the bloodserum.*" By Dr. J. E. G. VAN EMDEN. (Communicated by Prof. Th. H. MAC GILLAVRY.)

WIDAL and SICARD [3]) and also ACHARD and BENSAUDE [4]) have communicated that the bloodserum of patients suffering from febris typhoidea and that of animals, that had been rendered immune against the bacille of EBERTH, keeps its agglutinative power undiminished for many months; the agglutinines are so resistant that they do not perish even in mouldy and putrefying serum.

On the contrary I found that serum after some six weeks indeed

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[1]) Berl. Ber. XX S. 2530.
[2]) Berl. Ber. XX S. 301.
[3]) Annales de l' Instit. Pasteur XI p. 353.
[4]) BENSAUDE: Le Phénomène de l'Agglutination des Microbes. (Paris 1897).

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had lost a great deal of its agglutinative action: this at least was the case with sera from typhoid patients and from rabbits immunised against the *bacillus aërogenes.*

Also VAN DE VELDE[1]) had observed an important decrease of the agglutinative titre of serum that had been put away.

Stimulated by my[2]) communication VAN HOUTUM[3]) investigated two sera that had been kept five and eleven months in sealed glass tubes in the dark and at the temperature of the room: the agglutinative power had not diminished.

The disagreement in the results mentioned above must in my opinion be caused by differences in the ways in which the sera had been kept.

The tubes of VAN HOUTUM had been sealed, but my tubes — from which repeatedly a small quantity of serum was taken for testing purposes — were closed by cottonwool stoppers covered by pieces of paper or tinfoil.

Now the next experiment showed that the way of closing had a decisive influence on the fact whether the agglutinative power keeps constant or diminishes.

Serum of a known titre was kept in:

1	tubes	closed	by	cottonwool
2	„	„	„	cork
3	„	„	„	sealing
4	„	filled	with	hydrogen and sealed
5	„	„	„	carbon dioxide and sealed

Four months afterwards the agglutinative titre was determined again.

The agglutinative power of the serum in *all* the sealed and corked tubes had remained *unchanged.*

On the other hand in all the tubes closed with cotton wool the agglutinative power of the serum had strongly diminished, notwithstanding the clearly visible condensation — except in the case of one. This exception regards a soiled tube, in which the serum was covered by a layer of *mould*; this serum had also kept its power *unchanged.*

Conclusion. When the circulation of the air is hindered or suffi-

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[1]) Semaine médic. 1898 p. 379.

[2]) Nederl. Tijdschr. van Geneesk. 1898 II p. 342. Zeitschr. f. Hyg. und Infect. XXX p. 19.

[3]) „ „ „ „ 1898 II p. 841.

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ciently limited, the bloodserum keeps its agglutinative power longer than when the access of air is free.

It lies at hand to think here of the influence of the oxygen in the air and in fact, experiments not yet terminated, support this opinion.

Now it is important to investigate whether the unstability of the other specific substances occurring in the blood, especially the *antitoxines* must also be ascribed to the influence of the air. Perhaps that the efficiency of various medicinal sera will prove to be more durable, when they are kept in vacuo or in a neutral gas.

Geology. — "*The Amount of the Circulation of the Carbonate of Lime and the Age of the Earth*". I. By Prof. EUG. DUBOIS. (Communicated by Prof. J. M. VAN BEMMELEN.)

In a similar way as water is continually passing into the atmosphere, to return again to the earth, we find the carbonate of lime perform a circulation, as this matter is solved from limestone, and after having been carried to the ocean by the rivers, is there, through the agency of organic beings, again given back in solid state.

Even an approximative estimate of the amount of this circulation would be of considerable importance for geology, because we may regard it in connection with questions about the formation of that carbonate by decomposition of silicate rocks, and about the time required for its formation.

The results of an estimate as referred to, and some conclusions based on these results, are given in this paper, and in another paper I propose to present on the next occasion.

In investigating the amount of this circulation let us start from the carbonate of lime in the ocean.

The ocean contains in the deposits over its floor and floating about in the water such a vast amount of solid carbonate of lime, as remains of shells and skeletons of organisms, that, considering the perpetual movement, and the consequent mixing of the ocean water, we may take it for granted that, under the existing pressure of carbonic acid and the actual temperature of the atmosphere, it contains carbonate and bicarbonate of lime in saturated solutions.

From experiments kindly made at my request by Dr. ERNST COHEN in collaboration with Mr. RAKEN, and the results of which, are communicated to the Academy at the same time as this paper, this

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proved really to be the case. According to W. DITTMAR [1]) 0.345 pCt. of all the salts of average ocean-water are carbonate of lime. The relative quantity of salts being 0.035, which may be considered as the average salinity of the ocean [2]), 1 litre of ocean-water would then contain 120.7 mgrms. $CaCO_3$, of which 53.1 mgrms. CO_2 of normal calcium carbonate. From the average of 26 samples of water, taken from different parts of the ocean and at different depth, we may calculate 54.9 mgrms. CO_2 of normal calcium carbonate, and moreover 43.6 mgrms. of loose carbonic acid forming bicarbonate [3]). TORNÖE came to nearly the same results, as he found in the North Sea 53 mgrms. forming normal carbonate and 43 mgrms. of loose carbonic acid, forming bicarbonate [4]), per litre of water. With these the results of other analysts coincide. On account of the great uniformity of the chemical composition of the water of the ocean it may therefore be taken for granted, that in one litre of ocean water there are in solution on an average from 120 to 125 mgrms. carbonate of lime and of these about 100 mgrms. as bicarbonate. The investigation of Dr. COHEN shows that in artificial ocean-water, containing all the salts in the average quantity, as stated by DITTMAR, but no carbonate of lime, in a litre 125 mgrms. calcium carbonate could be dissolved from a surplus of suspended solid calcium carbonate by passing during a sufficient time a current of air, containing 0.00045 carbonic acid (a relative quantity in accordance with the average).

We may say, therefore, that in the ocean-water the aforenamed matter exists as a saturated solution under the given pressure of carbonic acid in our atmosphere, and therefore we must take it that all the carbonate of lime which the rivers carry incessantly to the ocean is a surplus.

A considerable amount of carbonate of lime is often to be found in the matter carried in suspension by large rivers to the ocean. Some analyses relating to this and extending over longer periods of time may be mentioned here. C. SCHMIDT [5]) found in twelve monthly determinations for the relative quantity of calcium carbonate in the suspended matter of the Amu-Darja from 17.0 to 19.6, on an average

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[1]) Report on researches into the composition of ocean water collected by H. M. S. Challenger. Challenger Reports, Physics and Chemistry. Vol. I. London 1884, p. 204.

[2]) DITTMAR l. c. p. 201.

[3]) l. c. p. 215.

[4]) Berichte der Norwegischen Nordmeer-Expedition. Abt. Chemie, referred to by BOGUSLAWSKI, Handbuch der Ozeanographie. Stuttgart 1884. Bd. I, p. 139.

[5]) C. SCHMIDT und F. DOHRANDT, Wassermenge und Suspensionsschlamm des Amu-Darja. Mémoires Acad. imp. St. Pétersbourg (7). Tome 25. n°. 3. 1878, p. 31.

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18.3 pCt., from which may be calculated an average quantity of 41.7 mgrms. of that salt per litre of water. BALLO [1]) found that from the 300 mgrms. suspended matter contained in a litre of Danube-water, 5.53 pCt. is lime combined with carbonic acid, being 9 pCt. or 27 mgrms. $CaCO_3$ per litre of water. The water from the Blue Nile near Khartoum, as the river was low or high, contained per litre 16.9 to 62.1 mgrms. solid calcium carbonate in suspension.[2]) The clay which the Nile deposits in its delta, according to different analysts contains 3.72 pCt. of this salt [3]), so, that taking into account the average quantity of solids in suspension of 458 mgrms. per litre [4]), the water of the Nile would have contained at the delta an average of 17 mgrms. calcium carbonate in suspension.

Where thus in many of the large rivers there is always a surplus of calcium carbonate, which may easily be acted upon by the dissolving agents, it is obvious that in these river waters too the solution must be saturated. Whereas however in the ocean-water this salt, as regards its absolute quantity, is of very little account in comparison with the other salts, in the water of such like rivers it constitutes nearly the half of all the salts which here form a much weaker solution.

According to a combination by Sir JOHN MURRAY [5]) of the analyses of 19 large rivers one litre of river water contains on an average 186 mgrms. of total sslids in solution, of which 79.6 mgrms. are calcium carbonate.

From the experiments of SCHLŒSING [6]), so highly important for geology, made in a similar way on pure water, as the recent experiment of Dr. ERNST COHEN on ocean-water, by bringing a large quantity of calcium carbonate in suspension in long contact with air, containing a constant relative quantity of carbonic acid, it follows [7]) that in one litre of pure water by common air, the pressure of carbonic acid being 0.0005, and 16° C temperature, 74.6 mgrms. carbonate of lime are soluble. The solution takes place for about 13.1 mgrms.

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[1]) Chemische Untersuchung des Wassers des Donaustromes bei Budapest. Berichte der Deutschen Chemischen Gesellschaft. 1878, p. 444.

[2]) A. CHÉLU, Le Nil, le Soudan, l'Egypte. Paris 1891, p. 25.

[3]) C. SCHMIDT, l. c., p. 40.

[4]) CHÉLU, l. c., p. 203.

[5]) On the total annual rainfall on the land of the globe, and the relation of rainfall to the annual discharge of rivers. Scottish Geographical Magazine. Vol. 3. Edinburgh 1887, p. 76.

[6]) TH. SCHLŒSING, Sur la dissolution du carbonate de chaux par l'acide carbonique. Comptes rendus de l'Académie des Sciences. Paris. Tome 74. (1872), p. 1552—1556, and Tome 75 (1872), p. 70—73.

[7]) L. c., p. 1555.

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as normal carbonate, independent of the pressure of carbonic acid and very little dependent on temperature, for a greater part however, namely 61.2 mgrms. as bicarbonate, the lime being combined with a double quantity of CO_2. The quantity of the bicarbonate thus formed depends, for a given temperature, on the pressure of carbonic acid. The value of the pressure of carbonic acid and of the quantity of carbonate forms two geometrical series, but the ratio of the former is greater than that of the latter series. If the pressure of carbonic acid were 0.0008, i. e. more than one and a half the actual pressure, the quantity of bicarbonate formed would be 73.2 mgrms. per litre of water. At a pressure of 0.05, i. e. the hundredfold of the pressure of carbonic acid in the atmosphere, the quantity of bicarbonate only increases to 349,3 mgrms. per litre of water, that is a little more than five times and a half (5.7). Generally stated the quantity of bicarbonate formed depends in such a way on the tension of carbonic acid, that, if that tension is called x, the quantity of the bicarbonate $y = \frac{x^{0,37866}}{0.92128}$.

So if the pressure of carbonic acid rose to 700 times that in the atmosphere the quantity of carbonate of lime dissolved in the state of bicarbonate would be only about twelve times as great as at the actual pressure of carbonic acid in the atmosphere, and that of the carbonate dissolved in both states, as normal carbonate and as bicarbonate, only about ten times as great as under the actual condition of carbonic acid pressure.

SCHLŒSING found moreover, that with every degree of variation in the temperature, the quantity of the bicarbonate dissolved varies about 1 pCt., viz: it rises as the temperature falls, and it diminishes as the latter rises.

The figures given by SCHLŒSING for the quantity of the carbonate of lime dissolved at the pressure of carbonic acid in the atmosphere and 16° C. temperature come so near the average quoted quantity of that matter in river water, which on an average has about the same temperature (the mean temperature at the surface of the earth being 15° C), that it may be taken for granted, that those large rivers keep the carbonate of lime in solution in similar way as in pure water, partly as carbonate, for the greater part however as bicarbonate, and that the quantity of that double salt in it is depending on the pressure of carbonic acid in the atmosphere.

The number of analyses, from which MURRAY drew the above mentioned averages seems to be sufficiently large for the purpose, nevertheless, when the existing reliable analyses of river water are compared

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with one another, it appears that these deviate rather strongly, and that the average has only this value, that on the whole the relative quantity of dissolved carbonate of lime oscillates about saturation with that salt in pure water under the pressure of carbonic acid in the atmosphere. In some cases the relative quantity observed remains below it, but mostly it rises higher.

In one and the same place the relative quantity of carbonate of lime dissolved in river water varies according to the water mark. If the river rises the quantity of suspended matter per litre of water increases, but the quantity of dissolved matter, and among these of carbonate of lime diminishes. A few examples may explain this.

According to the determinations of VOHL [1]) the quantity of carbonate of lime in the water of the Rhine, taken from the same place, a little above Cologne, varied from 52.37 mgrms. per liter at high water mark, to 109.37 mgrms. at low water mark, thus in the ratio 1 to 2. This diminution of the relative quantity of dissolved matter in general and of carbonate of lime in particular, when the discharge of water is greater than usual, is a fact generally observed, which, among others, has been sufficiently proved from long and reliable observations made on the water of the Danube by BALLO [2]) and WOLFBAUER [3]) and from the water of the Meuse by SPRING and PROST. WOLFBAUER found [4]) that the relative quantity of suspended matter in 23 determinations, made during a year with intervals of, on an average, 16 days, proved to vary from 9.6 mgrms. as a minimum to 331.3 mgrms. as a maximum per litre of water, which two numbers stand to each other in the ratio as 1 to 35, whilst at the same time with the given minimum of the quantity of suspended matter a maximum of dissolved matter of 207 mgrms. was obtained, and at the same time with the quoted maximum of the quantity of suspended matter a minimum of dissolved matter of 130 mgrms. per litre, which two numbers stand to each other as 1.6 to 1. Whereas during low water the Blue Nile near Khartoum, according to CHÉLU [5]) carries only 156.3 mgrms. and during high water 1673.4 mgrms. of suspended matter per litre of water, so in the ratio 1 to 10.7, the

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[1]) H. VOHL, Ueber die Bestandtheile des Rheinwassers bei Cöln. DINGLER's Polytechnisches Journal. Bd. 199. 1871. p. 311 sqq.

[2]) M. BALLO, l.c. p. 441—445.

[3]) J. F. WOLFBAUER, Die chemische Zusammensetzung des Wassers der Donau vor Wien im Jahre 1878. Sitzungsberichte der Math. Naturw. Classe d. Kais. Akad. Wiss. Wien. Bd. 87. (1887), p. 404—424.

[4]) l. c. p. 414.

[5]) l. c. p. 25.

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quantity of dissolved matter during high water was at the same time even a little higher than during low water, it rose namely from 201.4 mgrms. to 232 mgrms. per litre. The total solids in solution in the water of the Meuse at Liege attained during a year a maximum at low water mark of 279 mgrms. and a minimum at high water of 86.2 mgrms. per litre, giving a ratio of a little more than 3 to 1 [1]). For the matter in solution in the Arve the maximum is to the minimum in the ratio 2.5 : 1, whilst for the suspended matter this ratio was 5000 : 1. [2]).

However those extremes are only attained on one single day. Comparing longer periods of time we find the differences far smaller. For the Elbe in Bohemia the minimum quantity observed in 22 determinations, made during a year, amounted to 20.3 mgrms. Ca O, the maximum quantity to 45 mgrms. per litre of water, and the quantities of the other substances showed similar unimportant variations, [3]) whilst those of the suspended matter [4]) varied from 1.13 to 756.01 mgrms. per litre. WOLFBAUER corroborated moreover the fact, which had already repeatedly been noticed, that, no matter how much the absolute quantities of the dissolved substances may vary, the mutual ratio of the components remains almost unchanged [5]). Something similar is also known of the substances in suspension in the river water, and appears clearly from the twelve monthly analyses of the suspended matter in the Amu-Darja, published by SCHMIDT [6]). Silicates and quartz for instance varied in it only from 76.2 to 79.86 pCt. Hence follows, which is important for the following considerations, that the results of a single analysis may be applied to determinations of the absolute quantities of the same river.

Besides those variations of the relative quantity of suspended matter depending on variations of the water mark in connection with time, and which, as is generally observed, can in large rivers

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[1]) W. SPRING et E. PROST, Etude sur les eaux de la Meuse. Annales de la Société géologique de Belgique. Tome 11 (1883—1884). Liège 1883. p. 175.

[2]) B. BAËFF, Les eaux de l'Arve. Thèse. Genève 1891, p. 59.

[3]) F. ULLIK, Beobachtungen über die Bestimmung der während eines Jahres im Profile von Tetschen sich ergebenden Quantitätsschwankungen der Bestandtheile des Elbewassers und der von letzterem ausgeführten löslichen und unlöslichen Stoffe. Abhand. kön. böhmischen Gesellschaft der Wissenschaften. VI. Folge. 10 Band. Math. Naturw. Classe. N°. 6. Prag 1880, p. 31.

[4]) Ibid. p. 28.

[5]) l. c. p. 415.

[6]) l. c. p. 31.

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at most amount to the ratio 1: 3, and this very transitorily, variations have been stated of the relative quantity of carbonate of lime in solution in the rivers according to space. Some rivers have a lower average quantity of carbonate of lime than others, though with most large rivers those differences are not great, at most amount to about the same ratio as the temporary variations, which are of very short duration.

But also in the same river, and even over small distances, the quantity may be a little different. That was apparent again from the observations of VOHL. The water taken on the same day, but from three different points, namely above, in and below Cologne, as well during high as low water mark, proved to grow richer in carbonate of lime in its course through the town.

The quantity of carbonate of lime, in milligrammes, contained in one litre of water from the Rhine was,

	during very low watermark, on Oct. 21st 1870,	during high watermark, on Nov. 8th 1870,
above Cologne	109.37	52.37
in Cologne	115.78	68.92
below Cologne	123.44	108.68

This increase is evidently to be accounted for by the influence of organic matter, combinations of carbon, which pollute the water and are consequently oxydized in it, and which, as long as they remain there, keep more carbonate of lime, in the state of bicarbonate, in solution than the carbonic acid of the atmosphere, absorbed in the water, would alone be able to do. That really the organic substances in the river water are soon oxydized is evident from the fact, stated by ULLIK, that those substances soon diminish in water samples kept standing for some time. From the observations made by him [1]) is to be derived that on an average in 24 hours 3.5 pCt. (from 1.7 to 5.4 pCt.) of the organic matter is decomposed. Bacteria and algae are the principal agents and contribute mostly to the so called self-purifying of the rivers.

Very instructive in this respect are the analyses of the water of lakes as they have been stated principally by DELEBECQUE. From these it has been made evident, that the water of lakes fed by rivers and rivulets in a region rich enough in limestone, takes in general the more carbonate of lime in solution in proportion to the surface

[1]) l. c. p. 6.

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of the lake being smaller. The increase of the circumference indeed is less than that of the surface, it increases in general as the square root of the surface. A lake, whose surface for instance is the ninth part of that of another lake, has, if the two are uniform, still the third part of its surface. Moreover the depth also often decreases with the length and breadth, though by no means in the same proportion, so that the volume of water of a small lake in comparison with its circumference is a good deal less. Now as organic matter principally enters the lakes from the circumference, it is clear that by the continually flowing source of carbonic acid, which this matter produces by its decomposition, the quantity of carbonate of lime, in the state of bicarbonate, in the water of these lakes under otherwise similar circumstances is greater in proportion to the lakes being smaller. FOREL [1]) had already pointed out that in the mud at the bottom of a lake the quantity of organic débris is the greater in proportion to the lake being smaller. In the following lakes, investigated especially by DELEBECQUE [2]), all draining the same limestone regions, the influence of size is clearly to be recognized.

	Surface, in K.M².	Volume, in M³.	$CaCo_3$, in mgrms. per L.
Lake of Geneva [3])	582.40	88920000000.0	72.3
Lac du Bourget	44.62	3620.0	96.0
» d'Annecy	27.00	1123.5	123.7
» d'Aiguebelette	5.43	166.6	126.4
» de Paladru	3.90	97.2	150.9
» de Nantua	1.41	40.1	154.5
» de Sylans	0.50	4.8	152.6

Something similar is to be observed concerning rivers. At the same length a large river is less liable to pollution than a smaller one. The distance from Geneva to Lyons is less than that from lake Ontario to Vaudreuil (above Montreal), yet the Rhone to Lyons having the same length of bank and containing only $^1/_{45}$ of the water of the St. Lawrence river, takes more organic matter and in consequence of this the Rhone at Lyons [4]) held in winter 150, and in summer 100 mgrms. $CaCO_3$ per litre in solution, the St. Lawrence (March 30th)

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[1]) F. A. FOREL, Le Léman. Étude limnologique, Lausanne 1895. Tome II, p. 134.

[2]) Archives des sciences physiques et naturelles. (3). Tome 27. Genève 1892, p. 569—570 and p. 134. — Tome 28, p. 502.

[3]) From FOREL and DELEBECQUE (quoted afterwards).

[4]) According to BOUSSINGAULT and PASQUIER, quoted by G. BISCHOF, Lehrbuch der chemischen und physikalischen Geologie. 2 Aufl. Bd. I. Bonn 1863, p. 272.

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only 80.3 mgrms. [1]), whereas in the large lakes, whose outlets they are, there is only about as much $CaCO_3$ dissolved as in pure water.

Freshwater lakes with an outlet are of great importance in considering these questions, on account of the rather constant composition of their waters, which is a consequence of their volume being very large in comparison with that of the discharge of the affluents and of the outlet. The lake of Geneva contains about 11 times as much water as the yearly discharge of the Rhone at Geneva, lake Ontario 10 times as much water as is flowing every year through St. Lawrence river; the water of the lake of Annecy is on an average renewed in 3.3 years, and that of the lake of Paladru in 4 years [2]). So one single analysis of their waters has already a great value. The quantity of carbonate of lime in the water of some lakes must therefore been spoken of somewhat more in extenso.

Very large lakes, in the drainage area of which much limestone occurs, receive relatively to the bulk of their waters so little organic matter, and their relative quantity of carbonate of lime is therefore so greatly influenced by the pressure of the carbonic acid in the atmosphere alone, that it agrees nearly with that which SCHLŒSING stated for pure water. From 11 reliable analyses of the water of the lake of Geneva, which varies only a little in composition in consequence of the mixture being temporarily and locally less perfect, or by variations of the temperature and the pressure of the air, contains per litre in 175 mgrms. dissolved solid matter 74.9 mgrms. calcium carbonate [3]). In the opinion of DELEBECQUE [4]) the first named number is not right; as average of 33 determinations, quoted by him, we find 169 mgrms. dissolved solid matter per litre of lake-water, in which, therefore, 72.3 mgrms. calcium carbonate are contained. The volume of the water in the lake of Geneva being 89 $K.M^3$., at an average yearly discharge of the Rhone at Geneva of 8 $K.M^3$., the water remains in the lake, as has been already stated, for about 11 years. Therefore organic matter which the rivers carry into the lake and which enters it from the shore can hardly have any noticeable influence on the quantity of the calcium

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[1]) According to T. S. HUNT in: Geology of Canada. Geological Survey of Canada. Reports of progress from its commencement to 1863. Montreal 1863, p. 567. Also in Philos. Magazine (4). vol. 13, p. 239. The sample was taken at the Point des Cascades near Vaudreuil, on the 30th of March 1863.

[2]) FOREL, l. c. Tome I, p. 446, and DELEBECQUE l. c.

[3]) FOREL, Le Léman II, p. 587.

[4]) A. DELEBECQUE, Les lacs français. Paris 1898, p. 191 and 197–198.

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carbonate. In fact the water of the lake of Geneva contains only little organic matter, on an average 5.5 mgrms. per litre [1]), whereas rivers according to MURRAY's statement contain on an average 19 mgrms. In the water of the Danube WOLFBAUER found, it is true, only 5.6 mgrms., there is however still suspended organic matter, according to BALLO 20 mgrms. per litre, of which hardly any is to be found in the lake of Geneva. ULLIK [2]) stated during one year's observations, that the organic matter in the water of the Elbe got below 6 mgrms. per litre on three days only, he found for the minimum 5 mgrms., and for the maximum 22.6 mgrms. per litre.

The lake of Geneva, therefore, contains, in distinction from other lakes, which are smaller, but also situated in a limestone region, hardly more carbonate of lime in solution than that corresponding to the tension of carbonic acid in the atmosphere. If with DELEBECQUE we take that the latter contains 0.00029 of its volume carbonic acid, the average pressure of the air on the lake of Geneva being 730 mm., we find for the tension of carbonic acid 0.000424, and from the formula of SCHLŒSING we calculate that 70.5 mgrms. carbonate of lime can be dissolved, as normal salt and as bicarbonate, in 1 litre of pure water at 16° C temperature, therefore at the average temperature at the surface of the lake of Geneva of 9.6° C., 75 mgrms.

At the mean relative quantity of carbonic acid of the atmosphere on the northern hemisphere of 0.000282 Vol. pCt.[3]) and the mean pressure of the air, where the rivers flow into the ocean, of 762 mm. we find that 70.8 mgrms. calcium carbonate (in both states) are soluble in 1 litre of water. [4])

The great North American lakes, whose waters flow to the ocean through the St. Lawrence river, have 425 times the surface of the lake of Geneva and about 500 times its volume, and lake Ontario, the water of which flows directly into the St. Lawrence river, has 34 times the surface and 40 times the volume of the lake of Geneva. The St. Lawrence river discharging yearly 364 K.M^3. of water, lake Ontario would empty in about 10 years, if the water were not continually renewed. Under these circumstances, even on account of one single analysis it may be taken that the water of the St.

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[1]) FOREL, Le Léman, II p. 615.

[2]) L. c., p. 31.

[3]) A. MÜNTZ et E. AUBIN, Recherches sur l'acide carbonique de l'air. Mission scient. du Cap Horn 1882–1883. Tome III. Paris 1886, p. A. 82.

[4]) DELEBECQUE (Les lacs français, p. 218) arrives at different results by erroneously substituting the relative volume for the relative pressure.

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Lawrence above Montreal, to where only one single insignificant little river joined, and has only been in contact with cambrian and cambrio-silurian crystalline rocks, can only be very little richer in carbonate of lime than the water of the lake itself. Near Vaudreuil it contained in a litre, according to the modus of calculation, from 80.3 to 80.8 mgrms. carbonate of lime [1]). The relative quantity of that salt in the lake-water will therefore not differ greatly from that of Geneva.

The water of lake Peipus in Russia, another large fresh water basin (having 6238 KM^2. in surface and 12 M. as its greatest depth) contains, according to the analysis of C. SCHMIDT [2]), in summer 67 mgrms. $CaCO_3$ per litre.

The water of the lake of Gmunden or Traunsee in Upper Austria (having a volume of 2.3 $K.M^3$., and through which flows the Traun keeps in solution 64 mgrms. calcium carbonate per litre [3]).

In the drainage area of all the above named lakes limestone is largely represented. Moreover in the mud on their bottoms there is much carbonate of lime, and the waters of the affluent rivers carry on an average more of that salt in solution with them than the waters of the lakes contain [4]). In the mud of the lake of Geneva [5]) there is found a mean percentage of 27.8, a minimum of 14.9 carbonate of lime, that of the lake of Bourget [5]) contains 55.5 pCt., of Annecy 28 to 79 pCt.; of Aiguebelette 29.7 pCt., of Paladru 84.7 pCt., of Nantua 56.3 pCt., of Sylans 73 pCt. [6]).

It is therefore evident that those waters must be satured with $CaCO_3$.

In regard to the analyses of river water I refer to BISCHOF and ROTH in the first place [7]). Some reliable and especially important analyses may still be quoted here.

According to two analyses of VOHL [8]), one during high and one

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[1]) T. S. HUNT in: Geology of Canada. Montreal 1863, p. 566.

[2]) Bulletin de l'Académie impér. des Sciences St. Pétersbourg. T. 16. 1871. p. 192.

[3]) R. GODEFFROY, Ref. in Jahresbericht über die Fortschritte der Chemie für 1882, p. 1623.

[4]) According to DUPARC (Le Lac d'Annecy, Archives des sciences physiques et naturelles (3). Tome 31. Genève 1894, p. 197) the water flowing through 13 rivulets into the lake of Annecy contains on an average 199.1 mgrms. $CaCO_3$ per litre, that from the lake itself 50 mgrms. less. The surplus is consumed by algae, whilst calcareous, tufa is formed.

[5]) Calcu'ated according to 15 analyses mentioned by FOREL (Le Léman, I. p. 122 – 124).

[6]) Archives, Genève. Tome 27. p. 573 and Tome 31. p. 197.

[7]) G. BISCHOF, l. c. — J. ROTH, Allgemeine und chemische Geologie. Berlin 1879, Bd. I. p. 457 seq.

[8]) L. c.

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during low water mark, of the water from the Rhine, taken above Cologne (in and below Cologne a temporary increase of the quantity of carbonate of lime takes place) it contains a mean of 80.8 mgrms. $CaCO_3$ per litre. BISCHOF found during low water at Bonn 94.6 mgrms., GUNNING [1]) in February 1862 at Arnhem 87.5 mgrms. Some other analyses of water from the Rhine yielded figures slighly higher, for instance those of FREYTAG (above Cologne in 1853 and 1855) 132.3 and 134.1 mgrms. and of SAINTE CLAIRE DEVILE (1848 at Strassbourg) 135.6 mgrms. per litre (these analyses all quoted by VOHL).

The determinations of the matter in solution in the Meuse at Liege, daily made during a year by SPRING and PROST, and the analyses of those, collected in 13 periods differing according to the water mark, show that the Meuse contains on an average 90 mgrms. $CaCO_3$ per litre of water [2]).

According to the analyses by WOLFBAUER of 23 samples of water taken during a year with intervals of about 16 days, the water of the Danube above Vienna contains on an average 97.9 mgrms., according to one analysis of BALLO at Budapest (in the middle of November) 88.7 mgrms. carbonate of lime per litre.

The Embach above Dorpat and the Welikaja at Pskow, which both flow into lake Peipus, contain in summer, during low water, 88 resp. 82.5 mgrms. dissolved carbonate of lime per litre of water [3]).

The Syr-Darja (May 1878), according to an analysis by C. SCHMIDT [4]) contains 86.4 mgrms. $CaCO_3$ per litre water.

The Blue Nile near Khartoum has on an average, from an observation at high and another at low water, 77.5 mgrms. carbonate of lime in a litre of water [5]).

From the analyses of water of the Nile near Caïro published by CHÉLU [6]) it appears, that on an average (from twelve, monthly repeated, observations) among the dissolved matter 42.5 mgrms. Ca O

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[1]) J. W. GUNNING, Onderzoek naar den oorsprong en de scheikundige natuur van eenige Nederlandsche wateren. Utrecht 1853, p. 66. Also in Journal für praktische Chemie, Bd. 61 (1854), p. 139.

[2]) Calculated from the statements (l. c. p. 208 and 212) of the solid matter in solution carried during a year and the yearly discharge of water. — Four analyses of water from the Meuse by CHANDELON (quoted by BISCHOF) yield a mean of 86.3 mgrms., one of GUNNING (l. c.) at Grave 72 mgrms. per litre.

[3]) C. SCHMIDT in Bulletin de l'Académie imp. des Sciences St. Pétersbourg 1875. Tome 20, p. 134.

[4]) Mémoires de l'Académie imp. des Sciences St. Pétersbourg. (7). Tome 29, 1881, p. 25.

[5]) CHÉLU, l. c. p. 25.

[6]) L. c. p. 177.

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are found, which would correspond to 96.6 calcium carbonate per litre. Part of this lime, however, is combined with sulphuric acid, in what quantity cannot be stated from the other results of the analyses, which seem to be stated wrongly.

From the water of the Mississippi, which, being a very large river, with a drainage area equal to 16 times that of the Rhine, would be of great importance, I am acquainted only with two analyses, one by AVEQUIN [1]) and another by JONES [2]). According to AVEQUIN, in August 1856, 1 gallon of water from the Mississippi above New Orleans (at Carrolton) contained 7.307 grains of carbonate of lime and carbonate of magnesia; according to JONES near New Orleans 1 litre contained 92.8 mgrms. carbonate of lime and no magnesia. If now according to the usual ratio we reckon that one United States gallon is equal to 57750 grains it would follow from the analysis of the first named chemist that one litre of Mississippi-water then contained 126.5 mgrms. $Ca\,CO_3 + Mg\,CO_3$ in solution. If taking however with MELLARD READE that one gallon is equal to 56000 grains then the number for the dissolved carbonates would be 130.4 mgrms. Carbonate of magnesia being in every case only present in small quantities, the two latter numbers for the carbonates appear to agree pretty well with the result of the analysis of AVEQUIN. According to the values for the yearly discharge of carbonate of lime and the yearly discharge of water of the Mississippi, quoted by RUSSELL, a quantity of 75.5 mgrms. per litre is to be calculated [3]).

The average quantity of carbonate of lime of twenty rivers in North America, nearly all of which, however, are of very small size, and many draining regions poor in or even deficient of limestone, is according to RUSSELL 56.4 mgrms. per litre [4]).

Among the smaller rivers there are many, flowing over limestone or taking up the water of sources situated in limestone, which are very rich in dissolved calcium carbonate, partly because they contain spring water, not yet sufficiently ventilated, which has taken up carbonic acid under a higher pressure, and partly on account of

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1) A. AVEQUIN, Journ. Pharm. (3). Vol. 37 p. 258. (1857). Quoted by T. MELLARD READE in American Journal of Science. (3). Vol. 29. (1885), p. 291.

2) W. J. JONES, Report La. St. Board of Health 1882, p. 370, quoted by J. C. RUSSELL in: Geological History of Lake Lahontan, Monograph of the U S. Geological Survey, Vol. XI. (1885), p. 176, Table A.

3) l. c. p. 175.

4) l. c. p. 174.

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their being more polluted by organic matter. In their further course they lose much of their dissolved carbonates.

Here may still be remembered the 9 analyses of Thames water, quoted by BISCHOF [1]), which all show a high quantity of calcium carbonate, namely from 115.6 mgrms. to 205.4 mgrms. per litre, and also those of the water of the Seine at Paris, according to POGGIALE [2]) by whom during a year an average of 115 mgrms. was found, and according to ST. CLAIRE DEVILLE, who found 163.5 mgrms. per litre in the water of the Seine below Paris. These results indicate again the increase of the quantity of carbonates of lime in consequence of pollution of the water by organic matter [3]).

Some rivers, which flow for the greater part of their course over crystalline silicate rocks, and of which only few are of large size, are on the contrary poor in calcium carbonate.

From the water of the Rio de la Plata, a river which, as to the size of its drainage area, is only little inferior to the Mississippi, and which discharges more water, there exists according to MELLARD READE [4]) "a very exhaustive series of observations and analyses," made by JUAN J. J. KYLE, during 1872 and 1873 and the results of which he has published in a pamphlet of 11 pages in 1873 at Buenos Ayres, which to my great regret I have neither been able to procure, nor to read. As average quantity of solid matter in solution of fourteen analyses of water taken at different times, from April to June, in the neigbourhood and above the city of Buenos Ayres, MELLARD READE gives $^1/_{6143}$, and from two analyses in September $^1/_{3125}$. If we take the sixteen analyses to be of equal value we get a mean of $^1/_{6028}$ or 166 mgrms. per litre of water, figures which agree very well with those observed in most of the other large rivers. Starting from the last stated mean we may compute from the results of analyses of Rio de la Plata water, published by KYLE elsewhere [5]), that it keeps in solution only 23 mgrms. carbonate of lime per litre.

The Amazone, according to the analysis of one sample by P. S.

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[1]) l. c. p. 273 and 274.

[2]) Jahresber. der Chemie, 1855. p. 521.

[3]) H. M. WITT, On the variation in the chemical composition of the Thames water. Philos. Magaz. (4). Vol. 12. London 1856 p. 114—122, published a number of analyses of the water of the Thames at Kingston and at Chelsea, according to which e.g. with a relative quantity of 137.3 mgrms. calcium carbonate, 23.3 mgrms. of organic matter were determined.

[4]) l. c. p. 292.

[5]) Chemical News, Vol. 38 (1878), p. 28.

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FRANKLAND [1]), keeps as little carbonate of lime in solution, 27.5 mgrms. per litre.

The Dwina above Archangel has, according to one analysis by C. SCHMIDT, only 20.2 mgrms carbonate of lime in a litre of water [2]).

As to smaller rivers, for instance the water of the Hudson, calculated from an analysis by C. F. CHANDLER [3]) keep 42 mgrms. calcium carbonate per litre in solutions, and that of the Delaware, according to an analysis by H. WURTZ of a sample taken from the reservoir at Trenton [4]), 25 mgrms. calcium carbonate per litre. Such rivers poor in dissolved calcium carbonate are mostly of minor importance as to their discharge of water.

In regard to the rivers, in whose drainage areas limestone rocks abound, it appears from the above stated facts and considerations, that in the water which they discharge into the ocean, dissolved carbonate of lime is found in a ratio which on the whole is somewhat higher than that which would exist, if it were under the influence of the carbonic acid of the atmosphere only and it contained a surplus of solid carbonate of lime. In fact limestone being spread all over the earth, we may take for granted that the greater part of the river water flowing into the ocean has had an opportunity to get saturated with carbonates of lime. Those rivers in general contain during low water mark rather more carbonate of lime, whereas during high water mark the quantity of this matter may fall somewhat below the saturation-point of pure water. On the other hand some large and many small rivers, draining areas which are poor in or deficient of limestone, keep considerably less carbonates of lime in solution.

It appears, therefore, that we cannot be far from the truth if we assume that the water which the rivers carry to the ocean keeps on an average as much carbonates of lime in solution as pure water can contain, thus taking that the influence of the carbonic acid developed by the decomposing organic matter is counteracted by that of the temporary diluting during high water mark, and that of the river waters flowing directly into the ocean, which are poorer in carbonate of lime. The surplus which the organic matter gradually develops in the river-water can never cause the pressure of carbonic

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[1]) Quoted by MELLARD READE, l. c, p. 295.

[2]) Bull. Acad. imp. St. Pétersbourg. Tome 20 (1875), p. 152.

[3]) Report of the American Public Health Association. Vol. I, p. 542–543 (quoted by I. C. RUSSELL, l. c. p. 176, Table A).

[4]) Also quoted by RUSSELL, ibid.

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acid to rise high, as is already evident from the fact that in summer the quantity of calcium carbonates dissolved is by no means always greatest, the greater absorbing power at lower temperature is prevalent as a rule. The highest surplus is found in such profusely polluted waters as those of the Thames.

The total quantity of the water, which the rivers discharge yearly into the ocean has repeatedly been estimated, by E. RÉCLUS [1]) at 28000 K.M, by A. WOEIKOFF [2]) at 18800 K.M. [3]), by Sir JOHN MURRAY [4]), from the most reliable data, at 27000 K.M^3. and DE LAPPARENT and PENCK agree with MURRAY.

According to MURRAY's figures, if at the same time we take that the water which the rivers discharge into the ocean contains on an average 74 mgrms. of carbonate of lime per litre, we may calculate that two billion (i. e. 2×10^{12}) KG. of carbonate of lime, which as solid rock would have a volume of about three fourths K.M^3, forming a cube with more than 900 M. side, are yearly carried to the ocean in dissolved state.

Considering now that the ocean water is saturated with carbonate of lime, that the quantity of ocean water does not undergo perceptible changes, and that moreover it is wholly inadmissable that this yearly surplus should serve only or for a large part to increase the calcium sulphate of the ocean, the latter salt being found in it only in about the tenfold quantity of the carbonate of lime, and therefore only in 800.000 times as great a quantity as that of the aforesaid yearly surplus itself; these two billion KG. of carbonate of lime must pass every year from the liquid into the solid state. That this happens entirely, or at least principally, by the agency of organisms and as we now know for the greater part indirectly through calcium sulphate, is of no account here. That on the other hand this carbonate of lime, which in the ocean became solid again, will once be elevated by the endogene forces of our planet and changed into land, brought again into solution to take the same way, is to be concluded as well from the fact that we find already mighty strata of limestone in the archean formations and in all later formations, as from the fact that all rivers and lakes in whose drainage areas no limestone rocks are found, contain only little carbonate of lime

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[1]) La Terre. Vol. I. 4me Edition, p. 514—517.

[2]) Die Klimate der Erde. Jena 1887. p. 50.

[3]) l. c. p. 70.

[4]) A. DE LAPPARENT, Traité de Géologie. 4me Edition. Paris 1900, p. 232. — A. PENCK, Morphologie der Erde. Theil I, p. 273.

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in solution. The instances already quoted by BISCHOF of the Dee at Aberdeen, whose sources are situated in crystalline silicate rocks (granite) and which contained only 12.2 mgrms. calcium carbonate per litre of water and of the glacier-rivulet Möll at Heiligenblut and Oetz at Vent, which, flowing over crystalline shists, proved to contain only 8.4 and 4.5 mgrms. per litre resp. of that salt in solution, whereas on the contrary the Lutschine at Grindelwald, having limestone for its bed, contained even close at the glacier as much as 40.5 mgrms. [1]) may here be mentioned as a proof that by far the greater part of the calcium carbonate, which the rivers carry to the ocean originates from limestone mountains, which have been formed from calcium carbonate made already solid in the ocean in former times.

The Croton River (supplying water to the City of New-York), draining a region of archean rocks, has only 87.2 mgrms. of dissolved matter and 28.5 mgrms. calcium carbonate in a litre of water [1]).

The Ottawa, receiving the greater part of its waters, flowing through many small lakes, from a region of crystalline rocks, and also draining great areas of forest and marsh, contains in solution 24.8 mgrms. calcium carbonate and 16.4 mgrms. of organic matter per litre of water [2]).

The water from the Upper Bann in Ireland, before reaching Lough Neagh has been flowing over 50 KM. of granite, and contains only 17.7 mgrms. $CaCO_3$ per litre [3]).

The water of the Elbe, on reaching Tetschen, near the northern frontier of Bohemia, has been in contact chiefly with crystalline silicate rocks and sandstones, and only in the silurian basin of Prague and in the Cretaceous rocks of the northern part of Bohemia also with some limestones. It contains, according to the determinations, made by ULLIK in 22 periods during a year, only 67.5 mgrms. matter in solution per litre (besides the organic substances), of which 50 mgrms. are calcium carbonate. That is not more than about a half of what a river so profusely polluted with organic matter as the Elbe at Tetschen would be able to take, if its waters

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[1]) L. c., p. 275.

[2]) J. D. DANA, Manual of Geology. Fourth Edition. New-York 1896, p. 121, quoted from E. WALLER, water supply of New-York City, 1881 and C. F. CHANDLER in Johnson's Cyclopedia. Vol. IV. The water was taken from the reservoir supplying New-York City, itself supplied from the upper part of the drainage area of this small river.

[3]) T. S. HUNT in Geology of Canada. Geological Survey of Canada. Report of Progress from its commencement to 1863. Montreal 1863, p. 566. "The water was taken on the 9th of March at the head of St. Anne's Lock, and was remarkably free from any sediment or mechanical impurity."

[4]) HODGES, Chemical News, Vol. 30 (1874), p. 102.

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came so largely in contact with limestone as is the case with most of the large rivers. And so in the suspended matter there are hardly any traces of solid carbonate of lime, indeed less than 1 mgrms per litre of water [1]).

The contact with limestone rocks of the waters of the Moldau, a large tributary to the Elbe, having been still less above Prague, they contain even less than half the calcium carbonate of the Elbe at Tetschen [2]).

According to an analysis of water from the Uruguay River at Salto by KYLE (l.c.) it kept in solution per litre 10 mgrms., according to another analysis by R. SCHOELLER [3]) of the water from the same river below Fray Bentos 16.2 mgrms. calcium carbonate. The drainage area is almost entirely taken by sandstone rocks, which are very poor in lime.

In six little lakes of the granite region of the Plateau Central of France DELEBECQUE found only 18 to 77 mgrms. solid matter in solution in a litre, on an average 37 mgrms. [4]), whereas 14 lakes, equally small, in the département du Jura, where limestone rocks abound, held 108.6 to 195.6, on an average 147 mgrms. solid matter in solution [5]).

The lakes of Gérardmer, in the département des Vosges, and Issarlès, in the département Ardèche, whose drainage areas are situated in granite, hold per litre of water 5.9 and 10 mgrms. carbonate of lime in solution; those of Chauvet, Godivelle-d'en-Haut and Pavin (in Puy-de Dôme), situated in basalt, 6.8, 5 and 15.7 mgrms., whereas for the total of the solid matter in solution these lakes were found to keep 21.1, 27, 21, 18.3 and 79 mgrms. per litre of water [6]).

The Rachel-See, a little mountain lake, situated in the Bavarian Forest in cordierite-gneiss, and having an outlet, contains, according to the analysis of H. L. JOHNSON [7]) only 2.22 mgrms. calcium carbonate per litre of water.

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[1]) Calculated from the total of the solid matter in solution and in suspension yearly carried (l. c, p. 53) and the yearly discharge of water (l. c., p. 51). On its further course the Elbe has so much opportunity to dissolve different substances, especially carbonate of lime, that its water above Hamburg contains per litre 237 mgrms. of total solids in solution (PENCK, Morphologie der Erdoberfläche, Stuttgart 1894. I Theil, p. 309.)

[2]) According to 7 analyses by A. BĚLOHOUBEK (Untersuchungen des Moldauwassers) in Sitzungsberichte der K. Böhmischen Gesellschaft der Wissenschaften in Prag. 1876, p. 37.

[3]) Berichte des Deutschen chemischen Gesellschaft. 1887, p. 1786.

[4]) Archives etc. Genève 1892, (3) T. 28 p. 504.

[5]) Ibid. p. 503.

[6]) Calculated from the results of analyses, published by DELEBECQUE, Les lacs français, p. 202—203. See also, Carte Géologique de France au $^1/_{80000}$, feuilles Épinal, Le Puy et Brioude.

[7]) LIEBIG's Annalen der Chemie. Bd. 95 (1855), p. 230.

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The large lake Onega [1]), which is almost entirely surrounded by Finland granites and diorites, contains only 10.8 mgrms. calcium carbonate per litre of water.

The water of Lake Superior, whose drainage basin is composed of ancient sandstones, conglomerates and crystalline rocks, with very little limestone [2]), keeps only 30.8 mgrms. calcium carbonate, 45.7 mgrms. of total solids in solution per litre [3]).

Reindeer Lake, lying in the great archean area of Central Canada, north of Lake Winipeg, has only 29 mgrms. dissolved solid matter, of which only a slight trace of lime, in a litre of water [4]).

Lake Tahoe, amid the granitic and shistose peaks of the Sierra Nevada and overflowing in the Truckee River, has 72.3 mgrms. of dissolved solid matter, of which 23.2 mgrms. are carbonate of lime, in a litre of water [5]).

Other lakes, which receive their water entirely or for the greater part, from areas of glacial deposits, which consists, mostly of the débris of crystalline silicate rocks, diluvial regions, are equally poor in calcium carbonate. So the lake of Starnberg or Würmsee in Bavaria [6]), which holds in solution only 4.8 mgrms. calcium carbonate per litre of water, and Loch Katrine in Scotland, which according to the analyses of WALLACE [7]), contains in a litre of water only 2.7 mgrms. CaO, for the greater part still bound to SO_3, and of which the drainage area, according to the description of Sir JOHN MURRAY and F. P. PULLAR [8]) consists almost entirely of drift (clay, sand and gravel), by the side of shistose grit with some mica-shists and very little diorite, rocks, which do not contain carbonate of lime. The latter is also wanting in the mud on the bottom of that little lake [9]). Lake Wener has only 36.2 mgrms. and lake Wetter 51.7 mgrms. matter in solution per litre of water [10]). In the drainage area of both these Swedish

[1]) C. SCHMIDT, in Bulletin de l'Académie imp. des sciences. St. Pétersbourg. T. 28 (1883), p. 248.

[2]) R. D. IWING, The copper-bearing rocks of Lake Superior. Monographs of the U. S. Geological Survey. Vol. V. Washington 1883, p. 340.

[3]) Analysis in Geological on Natural History Survey of Minesota. Eleventh annual Report, p. 175, quoted by Warren Upham, The Glacial Lake Agassiz. Washington 1895. Monographs of the U. S. Geol. Survey. Vol. 25, p. 544.

[4]) From analysis by F. W. CLARKE, quoted by I. C. RUSSELL, History of Lake Lahontan, p. 42.

[5]) Geology and Natural History Survey of Canada. Report of Progress for 1880 — 1882, p. 6. H.

[6]) MENDIUS, in Jahresber. der Chemie für 1856 p. 765.

[7]) Report of the meeting of the British Association for the Advancement of Science, held at Manchester 1861. London 1862, p. 94.

[8]) Geographical Magazine. Vol. 25. 1900. Plate II.

[9]) L. c. p. 329.

[10]) A. ALMÉN in: Berichte d. Deutschen chemischen Gesellsch. Berlin 1871, p. 751.

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lakes by the side of crystalline rocks only diluvial soil occurs.

All the last named lakes are, in respect to their having an outlet and concerning their nearly constant composition, which is dependent on the chemical character of their drainage area, to be compared with the lake of Geneva and the other beforenamed lakes which are all rich in lime. Likewise the very large lake Baikal, through which flow the Upper Angara and the Selenga and which moreover receives some two hundred small rivers, and rivulets, and overflows in the tumultuous Lower Angara. As far as that region has been geologically explored, there are found in the draining area of lake Baikal, besides of some pleistocence formations, principally archean rocks, also, however, to relatively small extent, palaeozoit limestone. Calculated according to the analyses of SCHMIDT [1]) its water (taken in April 1877 from under the ice) keeps per litre not more than 40.1 mgrms. carbonate of lime in solution. Lake Tschaldyr in Armenia, another, much smaller lake, of about 150 KM^2 surface and likewise having an outlet, containing only lixiviation water from trachytes, kept in solution (28 July 1879) per litre 42.5 mgrms. calcium carbonate. This relatively high figure for a basin situated in silicate rocks may be explained by the continual movement of the shallow water of the lake by violent gusts of wind, which keep it troubled and of a milky colour [2]). In consequence of this the suspended detritus of the rocks can more easily be decomposed by water and carbonic acid.

According to the estimate of TILLO [3]), the crystalline silicate rocks occupy about $^1/_4$ of the land surface of the earth, surely a much larger surface than that which is occupied by the limestone rocks. As nevertheless the river-waters take their carbonate of lime by far the greater part from the limestone mountains, it follows that the making of calcium carbonate from calcium silicate is a much slower process than the solving of previously formed limestone, and that therefore the above calculated quantity of two billion KG. of calcium carbonate performs for much the greater part a real circulation, of which only very little is newly added carbonate, though all the calcium carbonate of the earth must gradually have originated from the decomposition of silicates.

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[1]) C. SCHMIDT in Bulletin de l'Académie imp. de St. Pétersbourg, Tome 24 (1878), p. 420.

[2]) C. SCHMIDT in Mémoires de l'Académie imp. de St. Pétersbourg (7). Tome 29. (1881), p. 46 and 48.

[3]) Comptes Rendus. Académie des Sciences, Paris 1892, p. 5.

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Chemistry. — "*The solubility of calcium carbonate in sea-water*". By Dr. ERNST COHEN and Mr. H. RAKEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

Whilst engaged in forming a theory on the age of the earth, it was of importance to Professor EUGÈNE DUBOIS to possess further data as regards the solubility of calcium carbonate in sea-water under the usual conditions of temperature and pressure.

It is at his request that we undertook a research in order to obtain those data.

The *modus operandi* was, that sea-water in contact with the atmosphere (having the normal amount of carbon-dioxide) was saturated with calcium carbonate and that after this point was reached, the amount of $CaCO_3$ dissolved in an aliquot part of the liquid was estimated by analytical means.

Arrangement of the Experiments.

We prepared some litres of sea-water accepting as its composition that found by DITTMAR [1]).

He finds the total percentage of salts to be 3.5 consisting of:

$NaCl$	77.758
$MgCl_2$	10.878
$MgSO_4$	4.737
$CaSO_4$	3.600
K_2SO_4	2.465
$MgBr_2$	0.217
$CaCO_3$	0.345 [2])
	100.000

The calcium carbonate was precipitated $CaCO_3$ previously tested for the absence of other carbonates. As the solubility is dependent on the temperature this had to be carefully regulated. The experiments were made at 15°, which temperature was kept constant within 0.03—0.05° for some months. For this purpose we employed a thermostat with a toluene regulator also a spiral of composition tube through which streamed the water from the mains. This tube was placed in the water of the thermostat. The cooling thus caused

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[1]) Report on the scientific results of the voyage of H. M. S. Challenger 1873—'76 1884, pag. 204.

[2]) The $CaCO_3$ was only added afterwards when determining the solubility.

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was automatically compensated for by means of a gas flame connected with the regulator.

In the thermostat in which a few puddle-boards were kept in motion by a HENRICI hot-air motor, were placed two bottles containing the sea-water with a large excess of $CaCO_3$. The bottles were closed by trebly-perforated corks. Through the first hole passed a glass tube down to the bottom of the flasks, through the second one a glass tube ending immediately below the cork. Through the third hole passed a thermometer. A current of air was passed through the tubes reaching to the bottom of the flasks; this current was always strong enough to thoroughly stir up the calcium carbonate. The air entered the room through a glass tube which was pushed through an opening of the window then passed through a meter in which its volume was measured and was then conducted through a spiral of composition tube 10 meter in length which was placed in the thermostat. In this manner it was heated to 15° before entering the sea-water.

The tubes which ended underneath the corks of the flasks were connected with a water-suction airpump which drew the current of air through the water.

A slight evaporation of the sea-water takes place which is but trifling as the air takes up water from the meter, but we have still taken notice of this and carefully marked the level of the liquids so as to be able to keep this regularly constant.

The time of saturation was varied in order to be sure that equilibrium had indeed set in. Therefore, an analysis was made after passing the air for 8 days and nights and another after the lapse of 17 days and nights; these gave the same results so that it may be taken for granted that 8 days and nights are already sufficient to reach a state of equilibrium.

From time to time the CO_2 of the air which had passed through was estimated. To do this, we interposed in the arrangement a large flask holding about 5 litres through which the air passed before reaching the meter. After $1—1^1/_2$ hour the CO_2 was estimated by shaking with standard barium hydroxide and titrating the excess with succinic acid. In calculating, due regard was paid to the temperature and pressure.

When the experiment was finished, the current of air was stopped and the $CaCO_3$ was allowed to deposit. Then the liquid was filtered at 15°.

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Analyse.

Under the circumstances described, there existed in the water [1]) after the experiment:

1. Carbon dioxide in the free state.
2. Neutral calcium carbonate.
3. Acid calcium carbonate.

Through the clear solution was now conducted a current of air which was completely freed from CO_2 by passing it through a 2 meter long tube filled with soda-lime and some washbottles containing aqueous caustic potash. On passing a neutral gas such as air, both the free carbonic acid and that of the acid calcium carbonate are expelled whilst neutral calcium carbonate is precipitated.

Specially conducted experiments, one of which lasted $4^1/_2$ and the other 100 hours, proved that after $4^1/_2$ hours the decomposition of the acid calcium carbonate and the expulsion of the carbon dioxide is complete.

The solution thus treated was now examined as to its amount of combined carbon dioxide ($Ca\,CO_3$) by decomposing this with hydrochloric acid and weighing the expelled CO_2 in soda-lime tubes, according to the method of KOLBE-FRESENIUS [2]) which was carefully followed in every particular.

Results.

300 cc. of sea-water were used for each analysis.

a. Solution of $Ca\,CO_3$ through which was first passed a current of atmospheric air for 8 days and nights and then a current of air free from CO_2 and saturated with water vapour, for $4^1/_2$ hours.

According to the indication of the meter, 41100 litres of air had passed through the solution in 8 days and nights which is about 108 litres per hour.

Three estimations of carbon dioxide made during this time on different days gave as result 0,0371, 0,0323 and 0,0290 per cent of CO_2 by volume.

Found 16,2 milligrs of CO_2 in 300 cc. of solution saturated at 15°, or 53.94 milligrs per litre.

b. Solution of $Ca\,CO_3$ through which was first passed a current of atmospheric air for 17 days and nights and then a current of air free from CO_2 and saturated with watervapour for 100 hours.

Found 17.2 milligrs in 300 cc. or 57.27 milligrs per litre. We, therefore, find that sea-water saturated at 15° with calcium carbonate

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1) Compare GMELIN-KRAUT, Handbuch Anorg. Chemie, Part 1, 358.

2) FRESENIUS, Anleitung zur quant. Chem. Analyse, Bd. I (1875) § 449.

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contains an amount of 55.6 milligrs of neutral-combined CO_2 per litre.

It now appears from the researches of JACOBSEN [1]), TORNØE [2]) and DITTMAR [3]) (CHALLENGER Expedition) that the amount of neutral combined CO_2 in sea-water varies from 52.8—55 milligrs. per litre.

Our research, therefore, leads to the result that sea-water is saturated with calcium carbonate.

Amsterdam, Chemical University Laboratory, March 1900.

Physics. — "*On the phenomena of condensation in mixtures in the neighbourhood of the critical state*". By Dr. CH. M. A. HARTMAN (Communication N°. 56 from the Physical Laboratory at Leiden by Prof. H. KAMERLINGH ONNES).

In a communication of DUHEM [4]) the hypothesis is laid down that in a mixture of two entirely miscible substances the experimental and the theoretical isothermals for one and the same temperature, situated between the temperature of the plaitpoint and that of the critical point of contact, intersect twice in the area of the unstable conditions.

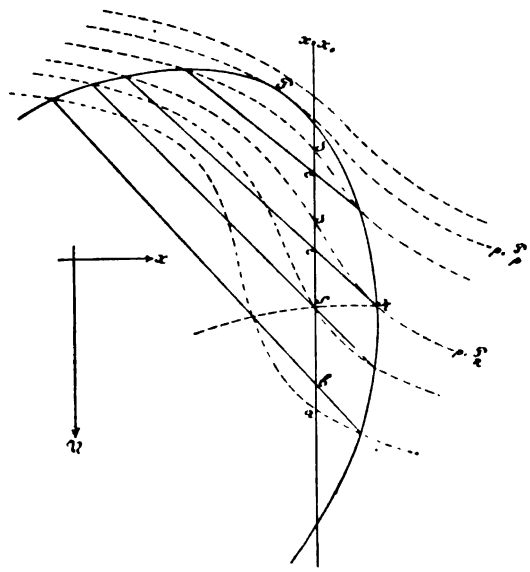

Fig. 1.

On p. 31 and in thesis I of my dissertation for the doctorate [5]) I have drawn attention to the fact that this hypothesis is at variance with VAN DER WAALS' theory of mixtures [6]).

The following may serve as a nearer explanation.

The actual condition may be seen from the annexed figure, derived from my dissertation in which the lines of equal pressure on the ψ-surface in the neighbour-

[1]) LIEBIG's Ann. 167. S. 1 (1873); Jahresbericht der Commission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel. 1872, S. 43.

[2]) Den Norske Nordhavs-Expedition 1876–78.

[3]) l. c.

[4]) Procès-Verbaux des séances de la Soc. des Sc. phys. et nat. de Bordeaux, 1899.

[5]) Metingen omtrent de dwarsplooi op het ψ-vlak van VAN DER WAALS bij mengsels van Chloormethyl en Koolzuur. Leiden, Juni 1899.

[6]) VAN DER WAALS, Arch. Néerl. XXIV, p. 1—56, 1889.

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hood of the area of the retrograde condensation are drawn projected upon the xV-plane.

That the course of the lines of pressure must be so, follows from VAN DER WAALS' formula, concerning all points of the connodal line in the ψ-surface:

$$\left\{\frac{V'-V}{x'-x}-\left(\frac{\partial V}{\partial x}\right)_p\right\}\cdot\frac{dP}{dx}=\frac{\frac{\partial^2\psi}{\partial V^2}\cdot\frac{\partial^2\psi}{\partial x^2}-\left(\frac{\partial^2\psi}{\partial V.\partial x}\right)^2}{\frac{\partial^2\psi}{\partial V^2}}$$ [1])

as has been explained on p. 30 of the dissertation.

As the second member of this equation is always positive (at the plaitpoint P it becomes zero, at the same time as $\frac{dP}{dx}$), the two factors of the first member have always the same sign.

In the critical point of contact R, where $\frac{dP}{dx}$ is infinitely great, the tangent-chord will touch the projection of the line of pressure.

Therefore in each point between P and R, where, as follows from the figure, $\frac{dP}{dx}$ is negative, $\left(\frac{\partial V}{\partial x}\right)_p$ will be greater than $\frac{V'-V}{x'-x}$, or in words: there the line of pressure will be steeper with regard to the x-axis than the chord.

At the other end of the chord, where $\frac{dP}{dx}$ is positive, the slope of the line of pressure will be less steep.

For pressures between P_P and P_R the lines of pressure in the unstable part lie therefore in projection between the chord and the connodal line, so that the projections of the chord and the pressure line for one and the same pressure between P and R cannot intersect.

For pressures lower then P_R the chord and the line of pressure will intersect in projection only in one point S. The line in which these points of intersection are situated extends over the whole breadth of the plait and terminates in the critical point of contact R.

If now we follow a line $x=x_1$ with decreasing volume, we shall

---

[1]) VAN DER WAALS, l. c. p. 15; in this formula a difference has been made between P the two-phase-pressure, and p the pressure in any point of the ψ-surface. V, x and V', x' then refer to the co-existing phases.

[2]) VAN DER WAALS, l. c. p. 56.

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be able to deduce the phenomena of condensation from the figure.

In the beginning of the condensation we shall for one and the same pressure first meet the line of pressure at a, then the chord at b, beyond S on the contrary, we first meet the chord at c and then the line of pressure at d.

If now we map the connection between V and p on a Vp-diagram, we shall refind the above-mentioned point of intersection for all mixtures, which show condensation, as the intersection of the experimental and theoretical isothermals, and this will be their only intersection. In the same way at the beginning of the condensation the first-mentioned isotherm will always be situated below and afterwards beyond the point of intersection always above the second.

2. DUHEM has arrived at his hypothesis in the following way:

First he traces how the total volume V_1 of a complex of two phases varies with the two-phase-pressure P, if the temperature remains constant.

Let x, V and m be the composition, molecular volume and quantity of the first phase (liquid), x', V' and $1-m$ those of the second phase (vapour), and x_1 the mean composition of the complex, then is

$$\left(\frac{\partial V_1}{\partial P}\right)_{x_1} = m \cdot \left\{\left(\frac{\partial V}{\partial p}\right)_x + \left(\frac{\partial V}{\partial x}\right)_p \cdot \frac{dx}{dP}\right\} + (1-m) \cdot \left\{\left(\frac{\partial V}{\partial p}\right)'_{x'} + \left(\frac{\partial V}{\partial x'}\right)'_p \cdot \frac{dx'}{dP}\right\} +$$

$$+ (V-V') \cdot \frac{dm}{dP}.$$

Now DUHEM considers what this relation becomes at the plaitpoint. Then

$$x = x' = x_1; \quad V = V'; \quad \left(\frac{\partial V}{dp}\right)_x = \left(\frac{\partial V}{\partial p}\right)_{x'} \text{ and } \left(\frac{\partial V}{\partial x}\right)_p = \left(\frac{\partial V'}{\partial x'}\right)_p.$$

Moreover he assumes, that here also $\frac{dx}{dP} = -\frac{dx'}{dP}$ and so concludes that $\left(\frac{\partial V_1}{\partial P}\right)_{x_1}$, $\left(\frac{\partial V}{\partial p}\right)_x$ and $\left(\frac{\partial V'}{\partial p}\right)_{x'}$ are equally great at the plaitpoint. He overlooks however that at the plaitpoint $\frac{dx}{dP}$ is infinitely great so that these quantities are not equal.

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In the plaitpoint therefore the experimental and theoretical isothermals in the Vp-diagram have not the same tangent, as has been wrongly drawn by DUHEM. Hence his further conclusions may be neglected.

3. Prof. VAN DER WAALS was so kind as to inform me that the mutual relation of the theoretical and experimental isotherms, and hence also the error of DUHEM's theorem, can be directly deduced from the sections of the ψ-surface and of the locus of the tangents-chords by a plane $x =$ const.

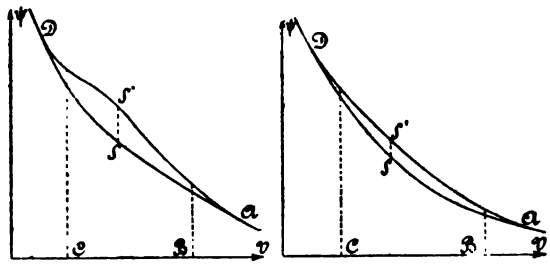

Fig. 2a. Fig. 2b.

For this Prof. VAN DER WAALS remarks: 1st. that — see fig. 2a and 2b [1]) where ψ has been taken as ordinate and V as abscissa — for a definite mixture the experimental ψ-line ASD must lie below the theoretical line $AS'D$.

2nd. that at the beginning and end of the condensation, at A and D, the experimental and theoretical ψ-lines have the same slope, and touch at those points.

3rd. that hence for a volume B in the beginning of the condensation the theoretical ψ-line has a greater slope than the experimental, or $P_{exp.} < p_{theor.}$ An equality of pressure for one and the same volume will again be attained where the tangents to the two ψ-lines become parallel, at S and S' in the figures. Again for a volume C near the end of the condensation the experimental ψ-line has a greater slope than the theoretical, or $P_{exp.} > p_{theor.}$

---

1) Fig. 2a relates to the case where the critical temperature of the mixture, supposed to remain of constant composition, lies below, and fig. 2b where it lies above the temperature, for which the ψ-surface is constructed; or: fig. 2a refers to values of x on one side, fig. 2b on other side of the straight line parallel to the V-axis and passing through K, the theoretical critical point on the ψ-surface, see Dissertation Pl. I fig. 5. K does not necessarily coincide with the intersection of tangent-chord and line of pressure.

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The points S and S' agree with the intersection of the two isothermals in the Vp-diagram, fig. 3^a and 3^b, and with the inter-

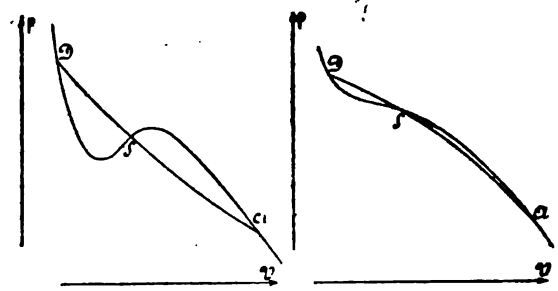

Fig. $3a$. Fig. $3b$.

section of the chord and the line of pressure in fig. 1. As no other cases than fig. 2^a and 2^b are possible there is only one such point.

4. With respect to the course of the condensation in the case of mixtures the following remarks may be added.

In the Vp-diagram the experimental isothermal can be either convex or concave towards the V-axis. The first is the case for a mixture which contains only a small proportion of the more volatile component, as occurs in VERSCHAFFELT's experiments [1]) — see fig. 3^a —. The second is the case for mixtures which consist principally of the more volatile substance, as occurs in KUENEN's experiments [2]) — see fig. 3^b —.

The experimental ψ-line will have its greatest curvature near D in the first case, near A in the second (comp. fig. 2^a with fig. 3^a and fig. 2^b with fig. 3^b).

Physics. — "*Measurements on the magnetic rotation of the plane of polarisation in liquefied gases under atmospheric pressure*". I. By Dr. L. H. SIERTSEMA (Communication N°. 57 from the Phys. Labor. of Leiden by Prof. H. KAMERLINGH ONNES).

1. The continuity of the optical properties of substances under different circumstances of pressure and temperature, especially during changes in the state of aggregation is an important point of investigation on which light can be thrown by measurements of the magnetic rotation of the plane of polarisation. If we calculate from the

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[1]) Versl. Kon. Akad. v. Wetensch. Amsterdam 24 Dec. 1898, p. 281; Proc. id. I, p. 288 and 323; Comm. Phys. Lab. Leiden, N°. 45.

[2]) Proc. R. Soc. Edinb. 21, p. 433, April 1897. Zeitschr. f. phys. Chem. 24. pag. 672, 1897.

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observations the molecular rotatory constant $\varrho_{p,t}$ [1]), this quantity will generally depend on pressure and temperature, and we can consider the manner in which it changes during the transition from the gaseous to the liquid state.

Measurements on this subject have been made by BECQUEREL and by BICHAT [2]) with Carbon disulphide and Sulphur dioxide as liquid and vapour. From these observations, in which no determinations of dispersion have been made, it follows that during the transition into the gaseous state the magnetic rotation of Carbon disulphide decreases much more rapidly than the density; and that BECQUEREL's formula $\frac{R}{n^2(n^2-1)} = \text{Const.}$ holds during the change of the state of aggregation.

My measurements on the magnetic rotation in gases [3]) led me into an investigation in this direction, which also was furthered by the ample means offered by the Leiden laboratory for experiments with liquid gases.

2. For the measurements of the magnetic rotation in liquefied gases under atmospheric pressure some special difficulties have to be surmounted. In the first place care must be taken that the cylinder containing the liquid, which must let through the pencil of light, shall be free from bubbles of gas which may easily be generated on the walls when they are not properly protected against the entrance of heat by conduction. Moreover this cylinder should be closed by plane parallel plates of glass of very good quality, as for these measurements it is difficult to place the nicols *in* the experimental-tube and thus within the closing-plates as could occur in the measurements on gases. These plates must also be protected against the entrance of heat but especially against moisture, as the least formation of ice on these plates hinders the measurements. This renders it necessary to place more than one set of glass-plates between the nicols, which latter circumstance again makes it necessary to use greater rotations than was required for the investigation with gases, as the glass-plates, good as they may be, render the adjustments less accurate.

3. The difficulties mentioned have been taken into account in

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[1]) Comp. Proc. Royal Acad. Amsterdam. Vol. I, p. 299.

[2]) BECQUEREL, J. de Ph. (I) 8, p. 198. BICHAT. J. de Ph. (1) 8 p. 204; 9 p. 275.

[3]) Proc. Royal Acad. Amsterdam. Vol. I, p. 296. Arch. Néerl. (2) 2 p. 291. Comm. Phys. Lab. Leiden, Suppl. 1.

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constructing the apparatus shown in figs 1 to 3, which consists of glass and ebonite only.

The experimental tube which is filled with the liquefied gas, consists of a glass tube *a*, closed by the glass-plates *b*, fastened to the tube by means of fishglue. By means of some brass collars *c*, acting as springs, a loose glass tube *d* lies in the experimental tube of the same length as the latter. The spaces within and round the tube are connected by means of the two obliquely ground ends at *E*. Through this tube *d* the pencil is directed during the measurements. The experimental tube is filled with the liquefied gas to a little above this loose tube, which thereby is filled with the liquid and entirely surrounded by it. Even supposing that a few bubbles of vapour arise on the walls of the experimental tube, they cannot get into the liquid contained in the loose tube and will not disturb our field of view.

The experimental tube is moreover surrounded by two glass tubes *f* and *g*. Through the openings *h* and *i* the cold vapour of the liquid in the experimental tube can stream successively through the two spaces formed by these glasses, and then escape through the india-rubber tube *k*, fastened to an ebonite ring *l* round the last named tube. The tube *k* conducts the vapour to a caoutchouc bag, in which it is collected provisionally, to be afterwards condensed. The liquid is admitted through an opening in the ebonite nuts *m*, which also serve to connect the various glass tubes.

To fill the tube we use the steel capillary *a* (fig. 3) which is put through the opening in the nuts *m* (fig. 1) so as to reach into the experimental tube, to which it is fastened by means of the cap *b* (fig. 2). When the tube is filled we remove this capillary and close the opening by means of a small stopper.

The two glass tubes *f* and *g* are closed by the ebonite caps *n*, in which caoutchouc rings *o* serve as washers. The caps are mutually connected by six brass tightening rods. The closing plates *b* of the experimental tube are kept in their places by means of the ebonite rings *p* in the caps *n*. These closing plates are shut off from the atmosphere by means of the glass-plates *q*, enclosed by the nuts *r* together with a leather packing *s*. These latter glasses are again protected against the formation of ice by spaces formed by them and the plates *t*, which spaces can be filled with dry air by means of the ebonite tubes *u*, or by placing some Phosphorous pentoxide into them [1]). The spaces between the glass-plates *b* and *q*

[1]) Comp. the Cryostate, Proc. Roy. Acad. Amsterdam, Sept. 1899.

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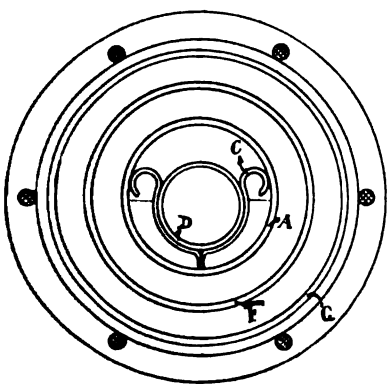
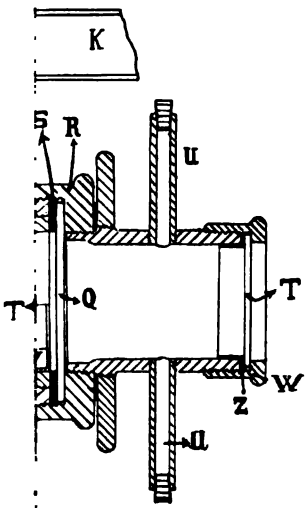
Fig 2.





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are also kept dry by means of Phosphorous pentoxide in ebonite cups *v*. The nuts *w* with leather packing and washers *z* serve to fasten the glass plates *t*.

4. The magnetic field is obtained by means of a coil with 24 layers of 46 turns of wire of 6 m.m. diameter, along which a current of as much as 70 amp. may pass. The direction of the current and the connection with the dynamo are arranged in the same way as for the investigation with gases [1]). Only the shunt [2]) is removed and replaced by a shunt of a WESTON-millivoltmeter, on which the strength of the current is directly read to within $^1/_{10}$ ampère, an accuracy quite sufficient for this case.

The apparatus described in § 3 is placed within this coil (inner diameter 14 cm.), and can be protected against the radiation of heat by means of a layer of wool or a water-circulation.

5. The optical arrangements also resemble in the main those formerly used for the investigation with gases. Here also the light of an arc-lamp, or of the sun passes successively through the collimator, the polariser, the experimental-tube, the analyser, the prism and the telescope. The rotations of the analyser can be measured by a divided circle, on which minutes can be read, and the adjustments are made by turning this analyser until the dark band in the spectrum has arrived at the desired place.

When we use the arc-light the spectrum is calibrated by causing the light of a mercury arc-lamp, following ARONS—LUMMER, to fall onto the collimator. By means of the spectral lines of this source of light and of the dispersion-curve of the prism determined with the aid of sun-light the telescope can always be adjusted for a definite wave-length.

6. Of all the observations with liquefied gases those with liquid methyl chloride offer the least difficulties. The following preliminary measurements are made with liquid methyl chloride purified by repeated distillation, under atmospheric pressure at —23°. From these measurements it can be shown that the dispersion is about the same as for most gases (comp. the curves and tables in the Proceedings Dec. 1898), as will appear from the following numbers.

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[1]) Comp. Proc. Roy. Acad. Amsterdam, Dec. 1898, fig. 1.

[2]) Comp. loc. cit. fig. 1. T.

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In this table ω/ω_D stands for the proportion of the rotation to that for sodium light.

λ	(ω/ω_D) CH_3Cl	(ω/ω_D) gases
0.631	0.90	0.87
0.546	1.17	1.17
0.480	1 58	1.53
0.449	1.76	1.76
0.435	1.90	1.90

Chemistry. — "*A new method for the exact determination of the Boiling-point*". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting).

Chemistry. — "*Thermodynamics of Standard Cells*" (2nd part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting).

Chemistry. — "*On the Enantiotropy of Tin*" (V). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

Chemistry. — "*The formation of mixture-crystals of Thallium-nitrate and Thalliumiodide*". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Will be published in the Proceedings of the next meeting.)

(June 30, 1900.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday June 30, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 Juni 1900 Dl. IX).

CONTENTS: "On the resisting power of the red bloodcorpuscles". By Dr. H. J. HAMBURGER, p. 76. — "The behaviour of mixtures of mercuric-iodide and silver-iodide". By Prof. H. W. BAKHUIS ROOZEBOOM, p. 84. — "A new method for the exact determination of the Boiling-point". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 86. — "Thermodynamics of Standard-Cells" (2nd part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 91. — "On the Enantiotropy of Tin". V. By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 93. — "The formation of mixed-crystals of Thalliumnitrate and Thalliumiodide". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 98. "Further researches on the formation of Indigo from the Woad (Isatis tinctoria)". By Prof. M. W. BEIJERINCK, p. 101. — "The amount of the circulation of the carbonate of lime and the age of the Earth". II. By Prof. ECG. DUBOIS (Communicated by Prof. J. M. VAN BEMMELEN), p. 116. — "Further results of an investigation of the Monotreme-skull". By Dr. J. F. VAN BEMMELEN (Communicated by Prof. C. K. HOFFMANN), p. 130 (With one plate). — "On soap solutions". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 133. — "Leperditia baltica His. sp., their identity with Leperditia Eichwaldi Fr. v. Schm. and their being found in Groningen diluvial erratics". By J. H. BONNEMA (Communicated by Prof. J. W. MOLL), p. 137. — "Contributions to the knowledge of some undescribed or imperfectly known fungi". (1st. Part). By Prof. C. A. J. A. OUDEMANS, p. 140 (With 3 plates). — "The motion of the Pole of the Earth according to the observations of the last years". By Dr. E. F. VAN DE SANDE BAKHUYZEN, p. 157. — "The properties of the pressure-curves for co-existing phases of mixtures". By Prof. J. D. VAN DER WAALS", p. 163. — "The HALL-effect and the increase of resistance of bismuth in the magnetic-field at very low temperatures". II. By Dr. E. VAN EVERDINGEN JR. (Communicated by Prof. H. KAMERLINGH ONNES), p. 177. — "On the system: Bi_2O_3—N_2O_5—H_2O". By Prof. J. M. VAN BEMMELEN, p. 196. — Prof. A. P. N. FRANCHIMONT presents the dissertation of Dr. L. VAN SCHERPENZEEL: "The action of hydrogen nitrate (real nitric acid) on the three toluic acids and some of their derivatives", p. 203. — "Thermodynamics of Standard Cells" (3rd Part). By Dr. ERNST COHEN (Communicated by H. W. BAKHUIS ROOZEBOOM), p. 208. — „The metastability of the Weston-cadmiumcell and its insuitability as standard of electromotive force". By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 217.

The following papers were read:

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Physiology. — *"On the resisting power of the red blood corpuscles"*. By Dr. H. J. HAMBURGER.

(Read March 31, 1900).

Since DUNCAN [1]) had in 1867 called attention to the fact that in chlorosis the red bloodcorpuscles lose colouring matter in a solution of salt, in which this does not take place under normal circumstances, MALASSEZ [2]) as a consequence of his study on the counting of the red bloodcorpuscles determined the so-called resistance of these cells, by mixing blood with a strongly diluted salt-solution and by examining at regular intervals how many bloodcorpuscles were left. The sooner the bloodcorpuscles were destroyed, the less the resistance.

Later on determinations of resistance were given by CHANEL [3]) equally by counting, although in a different way. Both methods are rarely cited even in French literature and still less put into practice. This is also the case with reference to the method of LANDOIS, LAKEN and also of others, who determined the power of resistance in regard to electric discharges, desiccation and other influences.

A more favourable reception was accorded to a method of investigation, originally only intended for the study of the laws of isotony in the bloodcorpuscles [4]) but which was first applied in 1890 by VON LIMBECK [5]) to investigate the resistance of the bloodcorpuscles during disease. It consists in the determination of the particular Na Cl-solution, in which the first bloodcorpuscles are about to lose colouring matter. If this happens for instance in a Na Cl-solution of 50 pCt., then 0.50 pCt. is called "the resisting power of the least resistant bloodcorpuscles".

If the dilution of the salt-solution is continued, a certain number of the more resistant bloodcorpuscles also lose their coloured contents, and finally all the bloodcells, even the most resistant, have lost these. In a salt-solution, somewhat stronger than the last one mentioned, the most resistant can thus still exist. It is this salt-solution which then represents the "maximum resistance" (MOSSO [6]),

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[1]) DUNCAN, Sitzungsber. d. Wiener Akad. d. Wissensch. 11 April 1867.

[2]) MALASSEZ, Mém. de la Soc. de Biol. 1873, p. 134; Compt. rend. de la Soc. de Biol. 1895, p. 2.

[3]) CHANEL, Sur la résistance des globules rouges. Thèse. Lyon 1886.

[4]) HAMBURGER, Kon. Akad. v. Wetensch. Proces-Verbaal der Zitting van 29 Dec. 1883. Archiv. f. (Anat. u.) Physiol. 1886.

[5]) VON LIMBECK, Prager med. Wochensch. 1890, No. 28 u. 29.

[6]) A. MOSSO, Archives Italiennes de Biol. 1887. T. VIII, p. 257.

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VIOLA [1]). With the methods here mentioned (HAMBURGER-MOSSO-VIOLA) a relatively large number of resistance-determinations have been made, but whether they have increased our knowledge of the physiological and pathological conditions, to the study of which they were applied, is very doubtful.

To a certain extent an exception might be made for cyanosis and feverish conditions. The observation that in cyanosis "decrease of resistance" is observed can at least be referred to the fact, that the same is seen in bloodcorpuscles treated with CO_2 [2]), and for this last symptom we have a good explanation [3]).

That the resistance must diminish in feverish conditions is evident when it is taken into consideration that in fever the proportion of alkali in the serum is lowered, which decrease also involves that the bloodcorpuscles belonging to it already begin to lose colouring matter in a higher concentration of salt than those which have sojourned in normal serum [4]).

The reason why the resistance-determinations referred to, have thus far had little success may be sought in the circumstance that it was not duly taken into account what was indeed obtained by determination of the resistance, and what was the physiological meaning to be attached to it. Even in 1895 one could read in the conclusions of the dissertation of URCELAY: "Sur la résistance de globules rouges", Thèse de Paris: "La cause de la résistance des globules rouges nous est inconnue", and this at a time, when most of the resistance-determinations thus far known had been performed and URCELAY had contributed some himself.

As regards myself, I never felt induced to use my method of investigation otherwise than for more circumscribed aims, and on purpose I have thus far avoided to use the *in casu* unfit word "resistance" when colouring matter disappeared under the influence of certain salt-solutions and other mixtures.

Being invited to read a paper on this subject in the International Medical Congress to be held in Paris next August, I find a welcome opportunity to study the question at the present time, the

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[1]) VIOLA, Gazette degli Ospedali 1894, p. 115; Archives de Physiol. et de Pathol. générale 1895, p. 37.

[2]) HAMBURGER, Versl. en Meded. Kon. Akad. v. Wet. 3e Reeks. Vol. IX. 1891, p. 197. Zeitschr. f. Biol. B. 28. 1892, S. 105.

[3]) HAMBURGER, Zittingsverslag Kon. Akad. v. Wet. 28 Nov., 1896; 24 Febr. 1897. Zeitschr. f. Biol. 1897. S. 252.

[4]) HAMBURGER, Versl. en Meded. Kon. Akad. v. Wet. 3e Reeks. Vol. IX, 1892, p. 354; Archiv f. (Anat. u.) Physiol. 1892, p. 513.

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more so because this affords a means of controlling the investigations lately made on the volume-determination of the protoplasmic reticulum of the bloodcorpuscles.

I shall try to analyse the term "resistance" of the bloodcorpuscles in regard to salt-solutions and must in the first place inquire which are the factors on which depends the loss of colouring matter in the bloodcorpuscles by means of salt-solutions. My particular view is, that the bloodcorpuscle consists of a protoplasmatic reticulum, the interstices or meshes of which, closed or unclosed, contain the intraglobular liquid; it is this liquid which solely represents the power of the cell to attract water; the protoplasmatic reticulum has no share in this.

If one now imagines a bloodcell being immersed in a hypisotonic solution, then only the contents of the meshes will swell. The amount of this swelling will be more considerable in a certain hypisotonic solution, the greater the amount of the osmotic pressure of the intracellular liquid and also the greater the quantity of the intracellular liquid in a given cell-volume.

The more considerable the increase in volume is, which the intracellular liquid can be made to undergo without colouring-matter being extruded from the protoplasmatic network, the more resistant the protoplasm may be considered to be.

Taking these matters into consideration, we conclude that when different salt-solutions are allowed to act upon the red bloodcorpuscles, three or perhaps two forms of resistance come forward.

1. *The resistance of the bloodcorpuscle against loss of colouring matter, under the influence of diluted solutions.*

It is this form of resistance, which has been determined until now. It is of a complicated nature.

2. *The relative resistance of the protoplasm against the extrusion of colouring matter during expansion.*

3. *The absolute resistance of the protoplasm against extrusion of colouring matter during expansion.*

Ad I. *Resistance of the bloodcorpuscle against loss of colouring matter in diluted salt-solutions.*

As it was observed above, it is this form of resistance which has hitherto been determined by the so-called method of the bloodcorpuscles.

To salt-solutions of gradually diminishing concentration a few

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drops of the same blood are added and it will be observed that in a Na-Cl-solution of 0.49 pCt. some colouring matter has been extruded, which is not the case in a Na Cl-solution of 0.50 pCt. This is called the minimum resistance. It would be more correct anyhow to express it by $\frac{1}{0.50}$, as the resistance is inversely proportional to the limit of concentration referred to; therefore in general $R_{(bloodcorpuscles)} = \frac{1}{C}$; in which C represents the limit of concentration, in which the first bloodcorpuscles are about to lose colouring matter. With regard to the application of this method we take the liberty to propose a modification. It seems to us to be recommendable, also in connexion with the determination of the other forms of resistance to perform the determinations in small funnelshaped tubes of which the capillary part is calibrated and closed with a little ebony stop. They have the same shape as described formerly[1]), but in view of their being used for human blood they are smaller. With a capillary pipette a determined quantity of defibrinated or oxalate blood is measured for the different tubes which contain an equal volume of the different salt-solutions and the mixtures allowed to stand for half an hour; they are then centrifugalized. After a quarter of an hour's moderate rotatory velocity the bloodcorpuscles have already subsided and it can be seen by comparison where colouring matter begins to extrude and where not. This way of experimenting has a threefold advantage.

1. As the relative quantity of blood and salt-solution has been fixed and also the shape and measures of the little funnel-tubes are equal, we can compare the results of different investigators better than could be done hitherto and uniformity is thus enhanced.

2. As the full subsidence need not be waited for, the time for the determination of the resistance will be shortened.

3. Those tubes of which it is desirable, can further be used for the determination of both the other forms of resistance; but later on more of this.

To find the maximum-resistance the same method is followed as for the minimum resistance: the salt-solution is determined, which, mixed with the blood, gives a perfectly pure transparent liquid. The solution, which yet retains a trace of opacity is the sought for C'_g.

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[1]) Verslag Kon. Akad. v. Wetensch. 21 April, 1897.

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The maximum-resistance is then $R'_b = \frac{1}{C'_g}$.

The average resistance $\frac{1}{2}(R_b + R'_b) = \frac{1}{2}\left(\frac{1}{C_l} + \frac{1}{C'_l}\right)$, whereas we shall call the difference $R'_b - R_b = \frac{1}{C'_l} - \frac{1}{C_l}$: resistance-breadth. The determination of this value seems important to me.

It ought to be kept in mind, however, that quantities of a complicated nature are here determined, which it can however be important to be acquainted with in certain circumstances.

Ad. 2. Relative resistance of the protoplasm R_{pr}.

It is measured by the proportion of the volume V_l which the intraglobular liquid may attain in maximo before it is exuded by the protoplasm, as compared to the volume (V_n), which it possesses in normal conditions.

This proportion $\frac{V_g}{V_n}$ can be found by means of three methods.

Method a.

This method consists in attempting to determine the limit-concentration of the Na Cl-solution, in which the bloodcorpuscle swells at its maximum (C_g), and is thus about to lose its colouring matter, and also the concentration of the Na Cl-solution, in which its volume remains unchanged, that is: a NaCl-solution C_n, isotonic with the serum. As the attraction exercised by the intracellular liquid towards water, agrees with that of its environment under different circumstances, so $\frac{v_l}{v_n}$ is $= \frac{C_n}{C_l}$, at least when the dissociation of the contents of the bloodcorpuscles and the surrounding Na Cl-solution are left out of consideration [1]).

For the determination of C_n the freezing-point-method can be used, or if only very little blood is available the method of GRIJNS-EYKMAN [2]).

Method b.

According to this method the quantity of water is determined with which the respective blood-serum can be diluted, without the

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[1]) This is permissible here, as will be explained elsewhere. Here this explanation would lead us too far.

[2]) C. EYKMAN, Annual report of the Laboratory for Patholog. Anat. and Bacteriol. at Weltevreden for the year 1894.

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blood losing any colouring matter. Let x be the percentage of the water added, then $\frac{v_p}{v_n} = \frac{100 + x}{100}$.

The quantity of serum required can be considerably limited, by centrifugalising each time blood has been added to the diluted serum and after having waited for half an hour. When by this time the red colour has not yet appeared a known quantity of water is dropped into this serum, it is mixed with the serum, and the serum thus diluted is brought into close contact with the underlying bloodcorpuscles. This is repeated until colouring matter is seen to be extruded. At the utmost 8 cc. of blood is needed for this method.

Method c.

According to a method formerly indicated by me, the volume of the protoplasmatic reticulum of a given quantity of bloodcorpuscles is first determined [1]). Let this be π. If further the volume of the bloodcorpuscles in their own serum be V_n, then the volume of the intra-globular liquid in the normal condition is $V_n - \pi$ and in the condition of maximum swelling $V_l - \pi$, and therefore the relative resistance $R_{pr} = \frac{V_l - \pi}{V_n - \pi}$.

With this method c the *average* relative resistance of the protoplasm is immediately fixed, the three values of V_g, V_n and π having reference to all bloodcorpuscles together.

For the two other methods mentioned sub 2 the resistance must be fixed separately, for the least resistant and for the most resistant.

If for method a the Na Cl-concentration, in which the most resistant bloodcorpuscles are about to lose the colouring matter, be C'_l, then the maximum resistance is $R'_{pr} = \frac{C_n}{C'_l}$, and the average

$$\tfrac{1}{2}(R_{pr} + R'_{pr}) = \frac{1}{2}\left(\frac{C_n}{C_l} + \frac{C_n}{C'_l}\right).$$

If for method b, x' be the percentage of water that must be added in order to extract colouring matter even from the most resistant bloodcorpuscles, then $R'_{pr} = \frac{100 + x'}{100}$.

The average resistance will then be:

$$\tfrac{1}{2}(R_{pr} + R'_{pr}) = \frac{1}{2}\left(\frac{100 + x}{100} + \frac{100 + x'}{100}\right) = \frac{1}{2}\left(\frac{200 + x + x'}{100}\right).$$

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[1]) Reports of the Roy Acad. of Sciences. Amsterdam May 28, 1898.

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The relative resistance breadth of the protoplasm we indicate by $R'_{pr} - R_{pr}$.

This value seems important from a physiological and pathological point of view.

Ad. 3. *Absolute resistance of the protoplasm against the extrusion of colouring matter during expansion* R_{pa}.

Superficially it might be supposed that the relation of the intracellular contents of the bloodcorpuscles in the condition of maximal swelling and in the normal condition, expresses the degree of resistance in an absolute sense. This however is not the case. Imagine two bloodcorpuscles of equal size in their own serum, both have intraglobular contents of equal osmotic pressure, but the volume of the intraglobular liquid is greater in the first bloodcorpuscle than in the second. If it is proved that, nevertheless, both bloodcorpuscles lose colouring matter in the same saltsolution (C_l), in which case the osmotic pressure of the intraglobular contents must necessarily be equal, then the conclusion is inevitable that the protoplasm of the first bloodcorpuscle is more resistant than that of the second, for the absolute increase of volume of the first bloodcorpuscle was more considerable than of the second. With equal C_n and C_l it is therefore not necessary that the resistance should be equal. In order to be able to compare the absolute resistance of the protoplasm of two bloodcorpuscles, the quotient $\frac{C_n}{C_l'}$, which was therefore called relative resistance, must be multiplied by a factor which expresses the percentage of the volume of the intraglobular liquid, a factor which we calculate from π.

$$f = \frac{V_n - \pi}{V_n} \times 100.$$

As we do not know whether this factor may be used separately with the minimum-resistance, or with the maximum-resistance because we do not know whether the relative volume of the protoplasmatic reticulum is the same in all bloodcorpuscles of the same blood, it is undoubtedly safer to use the factor only where it is in all cases applicable, viz. with the average resistance.

Thus in this third method the average absolute resistance of the protoplasm against the transmission of colouring matter when expanded is determined, so that $R_{pa} = f \frac{V_l - \pi}{V_n - \pi}$ (of method 2*a*).

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SIMULTANEOUS DETERMINATION OF THE THREE FORMS OF RESISTANCE.

Suppose the three forms of resistance have to be determined during an illness and little blood is thus at our disposal. 1 cc. of blood is taken, defibrinated and strained or made to flow in 0.2 cc. sodium-oxalate of 1.5 pCt. Of this blood equal quantities (measured with a capillary pipette) are transferred to little funnel-tubes, which contain NaCl-solution of 0.30, 0.32, 0.34, 0.36, 0.38, 0.40, 0.42, 0.44, 0.46 0.48, 0.50, 0.52, 0.54, 0.56 pCt. [1]).

These liquids are mixed, allowed to stand for half an hour and then centrifugalized. After this it is determined in which tube colouring begins to show itself. The tube following upon this containing a more concentrated liquid, represents C_l. By determining where the mixture has become transparent, the maximum-resistance C'_l is found. Thus $R_b = \frac{1}{C_l}$ and $R'_b = \frac{1}{C'_l}$ (Method 1).

Now five tubes are prepared with equal quantities of blood.

Tube (1), undiluted defibrinated blood.

" (2) blood + Na Cl 0.9 pCt. } to investigate in which Na Cl-solution the volume of the bloodcorpuscles becomes like that in tube (1).
" (3) " + " 0.88 "
" (4) " + " 0.86 "
" (5) " + the Na Cl-solution just found, viz. the limit solution C_l in which the bloodcorpuscles are on the point of emitting colouring matter.
" (6) " + Na Cl 1.5 pCt., also for the determination of the protoplasmatic reticulum.

The whole mass is centrifugalized to a constant volume.

We can now calculate the relative resistance $\frac{C_n}{C_l}$ by dividing the concentration of the Na Cl-solution (2), (3) or (4) by that of the Na Cl-solution (5) (Method 2*a*), or also by calculating the protoplasmatic reticulum π from the Na Cl-solution (2), (3) or (4) and the Na Cl-solution (6). Tube (1) gives V_n, tube (5) gives V_g, and therefore relative resistance R_{pr} is also $= \frac{V_l - \pi}{V_n - \pi}$ (Method 2*c*).

All the values are now also known for the calculation of the ab-

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[1]) If so many tubes are not to hand, the same could preliminarily be performed by increasing with 0.4 pCt. Na Cl and seeking whereabout the limits lie for minimum- and maximumresistance and then fix these more accurately later on.

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solute resistance, of which only the *average* can be determined. It is $100\, R_{pr} \frac{V_n - \pi}{V_n}$ (Method 3).

If there is reason to believe, in comparing the resistance of two samples of blood, that under normal circumstances the volume of the protoplasmatic reticulum, or, what comes to the same, of the intracellular liquid, does not differ, then the determinations become simpler and the results of 2a, 2b or 2c may prove to be sufficient. If moreover the osmotic pressure of the serum is the same, then the first method suffices.

Chemistry. — "*The behaviour of mixtures of mercuric iodide and silver iodide*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Read May 26, 1900.)

The double iodide $HgI_2\,2AgI$ is known as one of the finest examples of a solid substance which undergoes a change at a definite temperature, because this substance changes, when heated to 45°, from the pure yellow to orange red.

There was, however, a difference of opinion as to the change which takes place here; some attributed it to the change of the compound itself into another modification; others thought that, at 45° it broke up into the two component iodides.

At my request Dr. STEGER has made a further investigation of the matter and has come to the conclusion that the two iodides mixed in varying proportions and at different temperatures are of a very varying nature. If we start from fused mixtures, it appears firstly that the melting point of HgI_2 is lowered from 257° to 242° by an admixture of 14 mol. pCt. of AgI. On the other hand the melting point of AgI is lowered from 526° to 242° by an admixture of 86 mol. pCt. of HgI_2.

By means of an accurate determination of the temperature-interval in which solidification of a certain mixture takes place, it may be found out what happens during the solidification. To do this with accuracy, a bath was used of melted $NaNO_3 + KNO_3$ which was stirred and which by judicious heating enabled us to maintain any constant temperature between 200°—500°, or to slowly vary it. The course of solidification of the different mixtures shows that two kinds of mixed crystals are formed; on the HgI_2 side with 0—4 mol. pCt. of AgI, on the other side with 18—100 pCt. of AgI. The first series has the type of the rhombic HgI_2, the other

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that of the regular AgI which exist from their melting points down to 127° and 147° respectively.

After the solidification, there is therefore a hiatus in the mixing-series from 4 to 18 pCt. All intermediate mixtures consist, therefore, after solidifying of a conglomerate of the two limiting mixed crystals. Those of 4 pCt. undergo a change near 127° because the HgI_2 changes from the rhombic into the tetragonal form. The mixed crystals of 18 pCt. or more of AgI behave in a more remarkable way. Firstly, on cooling below 157° the mixed crystals having the composition $HgI_2 2AgI$ are suddenly changed into a compound of the same composition which is accompanied by a change in colour from pink to red.

This point of 157° is perfectly comparable with the solidifying point of a chemical compound deposited from a liquid mixture. But the analogy goes further. If a chemical combination can deposit from a liquid solution of the same composition, it can also do so from solutions whose compositions deviate in both directions, and the deposition then takes place at temperatures which are situated below the solidifying point of the liquid of the same composition. This also happens here. From mixed crystals which contain less AgI, the formation of the compound $HgI_2 2AgI$ occurs at temperatures which fall from 157°—118°; from those containing more AgI at temperatures from 157°—135°.

A further fall is impossible because at 118° and 135° two points appear, which present a perfect analogy with the eutectic points which are encountered when mixtures of liquids, which deposit only a single chemical compound, solidify. Just as in such points, the remaining liquid totally solidifies to a conglomerate of the compound with one or the other of its components, the remaining mixed crystals in this case form a conglomerate of the compound $HgI_2 2AgI$ with either HgI_2 or AgI.

In the case of liquid solutions the situation of the eutectic point is determined by the intersection of the line for the compound with that of the one or the other component.

The last mentioned lines then run as far as the melting points of the components.

Instead of these we have here the transition temperatures of HgI_2 (127°) and AgI (157°). The line for the transformation of mixed crystals into compound, therefore, meets on both sides:

1. The line for the transformation of regular AgI into the hexagonal form, which is lowered by admixture of HgI_2 from 147°—135°, the junction takes place here at 90 mol. pCt. of AgI.

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2. The line for the transformation of HgI_2 rhombic into the tetragonal form, which is lowered by admixture of Ag I from 127°—118°. This last line is, however, broken off because the mixing is not continual from 4—10 pCt. The exact composition of the mixed crystals at the eutectic point on this side is not yet known.

Below 118° and 135° all solidified mixtures are therefore transformed either into conglomerates of double salt with HgI_2 or with Ag I. Whether a small admixture of the other iodide in both iodides is possible is not yet quite certain.

When those conglomerates, on further cooling, arrive at 45°, the compound changes into another condition (from red to yellow), whether it is pure or mixed with HgI_2 or Ag I.

In agreement with this view it was found that the temperature at which this change took place was quite independent of the total amount of both iodides.

The most important result of the research is not however the correct interpretation of the last mentioned change which it affords, but the transformations which the mixed crystals, which are formed on solidifying, undergo between 157° and 118°.

We have here the second instance of mixed crystals changing into a chemical compound, the first instance having been observed by ADRIANI in the case of racemic campheroxim. We have, however, here the first instance of that change being connected with the change of both the components, which gives rise to a complete analogy with generally known phenomena of liquid solutions.

The discovery is particularly important because it concerns a connection between phenomena which I fancy also arise during the formation of mixed crystals from iron and carbon, but could not thus far be ascertained with certainty on account of the very high temperatures at which these changes occur.

Chemistry. — "*A new method for the exact determination of the Boiling-point*". By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read May 26, 1900).

Some time ago I described a very delicate method for the determination of the increase of the boiling point, in which the boiling took place in a silver apparatus the pressure being maintained constant. In many cases it is however an advantage to be able to

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use glass apparatus as we may then continually observe what is taking place.

I have, therefore, tried once more to satisfy the conditions required to obtain trustworthy results with a glass boiling vessel. The first condition is the removal of the danger of superheating and the second the prevention of perceptible radiation.

The easiest device for boiling a solvent or a solution without danger of superheating is undoubtedly to pass the solvent in the form of vapour through the solvent or the solution instead of heating directly with a flame.

This method has already been applied by LANDSBERGER [1]) to the determination of molecular weights. I have mentioned, previously, that I had already applied this method, but that the accuracy of the results was not satisfactory. As I noticed that one of the reasons of the less satisfactory results was a perceptible radiation of heat from the boiling liquid, I have had a piece of apparatus constructed by means of which this radiation can be reduced to a minimum in the simplest manner.

Description of the Apparatus.

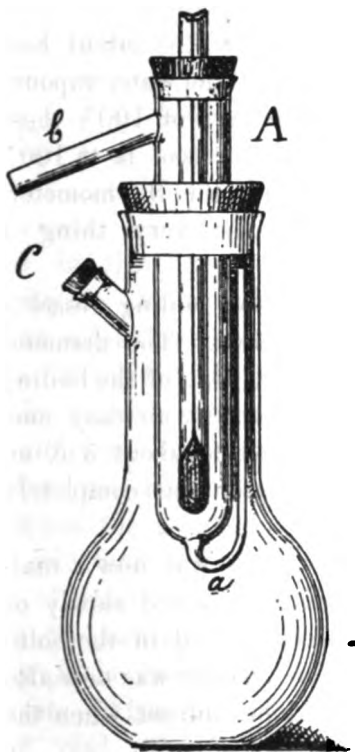

Fig. 1.

A is the boiling vessel, 180 m.m. long and 30 m.m. wide which is furnished at the bottom with a narrow tube *a* about 3 m.m. which is bent upwards and at the top with a wider side-tube *b*. This boiling-vessel is placed in a flask B with a long neck about 50 m.m. wide. The neck of this flask is furnished above with a side-tube *C*. The boiling vessel A may be fitted airtight into the neck of the flask B by means of a perforated cork cut in two halves.

After the flask B has been partially filled with water the boiling vessel A is filled with about 25 gr. of water and fitted airtight into the flask B by means of two half corks. The apparatus is now placed on a piece of copper-gauze and heated by means of an Argand-burner. The side tube *C* remains open until the water boils. When it

[1]) Zeitschr. f. anorg. Chem. 17 422 1889.

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is closed, the water-vapour escapes through the tube *a* and after having passed through the water in the boiling vessel it leaves the apparatus through the tube *b*. So long as the temperature of the water in the boiling vessel lies below the boiling temperature, a perceptible condensation of water vapour will take place which continually decreases until the water in the vessel A also boils. After 1 or 2 minutes, the water has reached a constant boiling point. Neither a reinforcement of the current of water vapour, nor a displacement of the thermometer has now any influence on the indication of the thermometer provided a strong current of vapour passes through the boiling liquid. From the latter it, therefore, appears that the mixing in this case neutralizes the difference in temperature of the different aqueous layers.

The result was somewhat different when I experimented with a solution. I noticed in this case that the indication of the thermometer was affected by an increase or decrease of the current of water vapour. The peculiar thing was that the stronger the current of water vapour became, the lower the indication of the thermometer. It struck me that this phenomenon must be explained as follows:

Water vapour may heat a solution, the boiling point of which lies above 100°, to its boiling point in consequence of the latent heat of evaporation set free during the condensation of the water vapour; as however the vapour bubbles have the temperature of 100°, these when in contact with the thermometer will tend to cool it to 100°. The more water vapour comes in contact with the thermometer, the greater will be the cooling and this is the very thing I observed.

To eliminate this error I introduced into the boiling vessel a cylinder of platinum gauze which was closed below. The diameter of this platinum gauze tube was rather less than that of the boiling vessel in order to render the passage of the current an easy one. The height of this platinum gauze tube amounted to about 5 c. m. so that the mercury reservoir of the thermometer was completely surrounded by it.

This arrangement produced the desired result; it was now a matter of complete indifference whether the current passed slowly or rapidly through the solution. The thermometer placed in the solution did not seem to be affected thereby. The mixing was now also complete as no difference in temperature could be noticed when the thermometer was displaced.

Whilst nothing special is noticed in determining the boiling point of water, and the duration of the experiment has no influence on

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the reading of the thermometer, this is not the case with solutions, because the concentration is continually changing owing to the condensation which takes place.

The largest quantity of water-vapour is condensed in unit time during the heating to the boiling temperature. Once the boiling temperature is reached, the condensation is at its lowest, and amounts to so little in the apparatus just described that the boiling point remains constant within 0.001° for about 3 minutes. The effects of the dilution then become perceptible and the boiling point slowly falls as is apparent from the graphical representation.

It is clear that the concentration of the liquid at the time when the boiling point has been constant for the half of 3 minutes, or one minute and a half, is nearest the concentration which corresponds to the recorded maximum temperature.

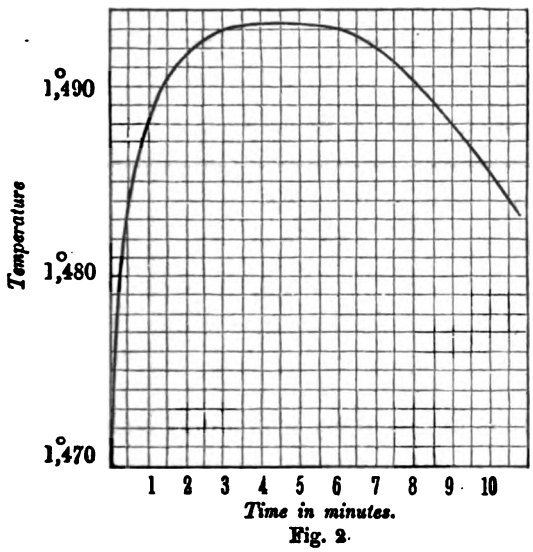

Fig. 2.

After the temperature has therefore remained constant for $1^1/_2$ minute, the experiment must be stopped and the concentration determined. As each experiment only takes a few minutes, the manostat need not be used in these observations. If two of the apparatus described are employed, and water is boiled in one of them, the slight error which might be caused by small variations in the atmospheric pressure during the short duration of the experiment may be eliminated. If the highest attainable accuracy is not desired, a single apparatus is sufficient, but then it is necessary to determine the boiling point of the pure solvent before taking in hand a fresh solution.

When the boiling point of the water (solvent) has been read off, the side tube *C* is opened and after the thermometer has been taken out of the bath, a weighed quantity of the substance is introduced into the boiling vessel. After putting back the thermometer, the flask *B* is heated and the side tube *C* is closed when boiling has set in. When the maximum boiling temperature of the liquid has been read off, the side tube *C* is quickly opened, the tube *B* is closed with an india-rubber cork, the boiling vessel is taken out of the flask and after a slight cooling it is attached with its thermo-

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meter to a balance showing accurately 0.01 gram and then weighed. No vapour can escape during the cooling as air bubbles are constantly entering from outside through the tube *A*. After every addition the same manipulation is performed.

If the boiling vessel and thermometer has been weighed when empty, the concentrations of the different solutions will be known.

I have determined the increase in boiling points of solutions of NaCl using a single apparatus and consequently working under the least favourable conditions and have found the following.

Na Cl.

Concentration.	Increase of Boiling point.	Molecular Increase of Boiling point.	i.
0,0617	0,065	10,5	2
0,1277	0,119	9,40	1,81
0,5590	0,520	9,30	1,79
1,1180	1,122	10,04	1,931

From this table it follows that the accuracy which may be obtained with a single boiling apparatus is great enough to demonstrate the peculiar progressive change of the molecular elevation of boiling point and of *i* with solution of Na Cl. The minimum of *i* lies here also between 0.1 and 0.5 gram molecule as was found with the silver boiling apparatus. As I have already stated, the accuracy is greater when two boiling vessels are used, one of which is always filled with water so as to eliminate the error caused by small changes in the atmospheric pressure.

It appears to me that when used in this manner, the apparatus gives more accurate results than that of BECKMANN which moreover has the disadvantage of being very complicated.

The new apparatus will be very suitable for collecting data for dilute solutions. It is less suited for the determination of the molecular weights of substances in non-aqueous solutions because the condition of its accurate action is the use of a perfectly pure solvent, as this, if impure does not have a constant boiling point when continuously boiled.

After I had already made a few preliminary experiments with the new apparatus, an almost identical arrangement was described

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in the "American Chemical Journal" April 1900 by H. N. Mc. Coy. The resemblance is striking, the only difference is that the tube *a* through which the vapour passes into the solution has been placed by Mc. Coy inside the vessel *A*, whilst in my apparatus it is situated outside it. Mc. Coy, has not however taken the precaution to prevent the vapour coming into contact with the thermometer and this, as we have seen, is very essential, if great accuracy is to be attained, as only then the boiling temperature is independent of the degree of heating of the flask *B*.

Amsterdam, University Chem. Lab. May 1900.

Chemistry. — "*Thermodynamics of Standard Cells*" (2nd part). By Dr. Ernst Cohen (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Read May 26, 1900).

1. In the first paper on this subject [1]) I have shown that the ideas prevailing on the reactions which take place in the standard cells are incorrect and ought to be replaced by others.

With the Clark-normal cell, a very satisfactory agreement was found between the theory and the measurements.

Before subjecting the existing data of the Weston-normal cell to calculation in an analogous way, a calculation which as will appear later on, is more complicated than for the Clark-cell, I would like to further explain a few points about the latter.

2. In the theory and in the calculation in the previous paper it was assumed that the cell was built up as follows:

$$Hg—Hg_2SO_4 \text{ — saturated solution of zincsulphate — } Zn$$

whilst for the calculation measurements made with cells of the following construction were used;

$$Hg — Hg_2SO_4 \text{ — saturated solution of zinc sulphate — zinc amalgam,}$$

about which it may be observed that the amalgam was composed of 1 part of zinc to 9 parts of mercury [2]).

We may now inquire whether such cells may be theoretically treated as if the negative pole consisted of pure zinc. It has already

[1]) Proc. Roy. Acad. Amsterdam. 1900, pag. 719.

[2]) Compare Kahle, Wiedemanns Annalen, 51. 205 (1894).

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been shown by LINDECK [3]) in 1888 that zinc and zinc amalgam show, towards solution of zinc sulphate, the same potential difference when a certain minimum of about 2 per cent of zinc in the amalgam is exceeded.

The zinc amalgam used in the CLARK-cells, therefore, behaves like pure zinc. That the presence of mercury exercises no influence is shown, moreover:

a. from the observations of KAHLE who showed that cells constructed with an amalgamated zinc rod instead of a 10 per cent amalgam showed an E.M.F. which differed by less than 0.2 millivolt from that of the amalgam cells; it may be observed that in these cases the amalgamation had taken place but very superficially.

b. From the communications of CALLENDAR and BARNES [1]), who have always worked with an amalgamated zinc rod instead of the amalgam and have still obtained results perfectly identical with those of KAHLE.

3. In the amalgam-cells, a new link enters into the mechanism, because on the passing of 2×96540 coulombs, the zinc must be first abstracted from the amalgam before it can unite with SO_4 to $ZnSO_4$ which then undergoes the hydration which has been discussed in the previous paper.

That the evolution of heat involved in the abstraction of zinc from the amalgam is of no importance, is shown from the fact that the E.M.F. and the temperature coefficient are exactly the same for the amalgam cells and for those where a superficially amalgamated zinc rod is employed.

4. It appeared to me of importance to lay stress on the foregoing, as in contrast to the zinc amalgams, the cadmium amalgams behave quite differently and this becomes important in the application of my theory on the WESTON-standard cells in which the negative electrode happens to be formed by cadmium amalgam.

I hope to make more extensive communications on the theory of these standards as soon as I have experimentally determined the required data.

Amsterdam, University Chem. Lab. May 1900.

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[3]) WIED. Ann. 35, 311 (1888).

[4]) About the diluted amalgams, compare LINDECK, l. c. 324. Also RICHARDS and LEWIS, Proc. American Acad. of Arts and Sciences. Vol. XXXIV 87 (Dec. 1898). Zeitschrift für phys. Chemie 28. 1 (1899).

[1]) Compare my first paper.

[2]) Compare WIED. Annalen 65, (1898) 926. CROVA, Ann. de chim. et de physique (3) 69, 458 (1863) had already found that if in a DANIELL-cell the zinc is replaced by zinc amalgam, the properties of the cell thereby undergo no change.

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Chemistry. — "*On the Enantiotropy of Tin*" (V). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read May 26, 1900.)

1. In the second and third communications on the peculiar conduct of tin, mention was made of the velocities with which the reactions

white tin → grey tin
and grey tin → white tin

occur at different temperatures.

It was then established that the change of the white modification into the grey one shows a maximum velocity at about — 48°, while above the transitiontemperature there was, as might be expected, no question of the appearance of a maximum.

I have now studied more in detail the velocity of change at different temperatures which has brought to light a number of interesting points which I will discuss in this paper.

2. I had filled a large dilatometer with about half a kilo of white tin filings which were inoculated with grey tin and in contact with a 10 per cent solution of pink-salt in absolute alcohol. This dilatometer was kept for three months in brine, the temperature of which varied from — 4° to — 7°.

After the lapse of this time small quantities of white tin were still observable between the grey mass in the dilatometer. I now proposed to keep the dilatometer at — 45° until, at that temperature, no change should take place in the level of the liquid in the capillary tube; I could then be certain that all the white tin had changed into the grey modification. A very narrow capillary was selected. By weighing out with mercury, the volume of 1 mm. in length was found to be 0.00037c.m. so that a displacement of 1 mm. showed the change of 10 milligrams of white tin into the grey modification if we still accept provisionally 7.3 and 5.8 as the respective sp. gr. of those modifications.

In order to maintain the temperature at — 45° for a long time, I made use of liquefied ammonia which may be strongly recommended for such purposes. A wide mouthed stoppered bottle, holding one litre, was nearly filled with the liquefied gas and introduced into a somewhat wider battery glass, on the bottom of which some corks were placed; the air surrounding the bottle forms a first-rate isolation. The whole was now placed in a box filled with bran.

The bottle was closed by means of a trebly-perforated cork; one

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hole served to admit the dilatometer-capillary, through the other passed a thermometer and through the third a glass tube, ending just underneath the cork, the other end of which passed through the window outside the room.

When the surrounding temperature was about 15°C., I only needed to add about 50 grams of liquefied gas every 24 hours to keep the dilatometer quite immersed. It very soon became apparent that the rate of change at — 45° was extremely small which seemed to me to contradict the results previously obtained. (Compare *Proc. Roy. Acad. Amsterdam.* 1899 102 also *Zeitschr. für phys. Chemie* **30**, 616). The research in this direction was consequently undertaken on a more extensive scale.

3. The large dilatometer was opened, the tin was carefully washed with dilute hydrochloric acid (the temperature was continually kept lower than the transition point), then with alcohol and ether and finally dried in vacuo over sulphuric acid [1]).

4. In order to be able to investigate afresh the velocity of the change, white tin→grey tin, I filled a dilatometer (A) with 43,9334 grams of the preparation, the purification of which has just been described and in which a certain amount of white tin was still present; 1 mm. increase in the capillary represented a change of 14 milligrams of white tin into the grey modification. As measuring liquid a 10 per cent solution of pink-salt in absolute alcohol was employed. The observations were now made in the following manner: to study the velocity at a very low temperature, I first placed the dilatometer in a bath of melting ice and water, which was vigorously stirred by means of a WITT's stirrer connected with a HEINRICI's hot air motor, and then read off the level of the liquid in the capillary. The dilatometer was then placed in the cooling bath (solid CO_2 and alcohol, liquefied NH_3, different cryohydrates) and left there for definite periods. It was then again put back into the ice-bath and the level of the liquid read off. By this method of working we become independent of small variations in the temperature of the low-temperature bath, which is very necessary, as the dilatometer acts also as an extremely delicate thermometer.

5. Working in this way, the results with dilatometer A were:

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[1]) The pink-salt was entirely removed in this manner; on shaking with water no chlorine reaction could be got with silver nitrate.

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TABLE I.

Temp.	Velocity of change.	Time of observation in hours.	Temp.	Velocity of change.	Time of observation in hours.
0°	14 mm.	2	—45°	0.4 mm.	$6^5/_6$
—45°	0.16 mm.	$15^2/_3$	0°	0.48 mm.	$16^2/_3$
0°	12 mm.	$4^5/_6$	—15°	0.43 mm.	7
—15°	3 mm.	$2^1/_7$	0°	0.45 mm.	$17^1/_2$
0°	12 mm.	$4^1/_2$	—85°	0.00 mm.	4
0°	5 mm.	$17^2/_3$	0°	0.50 mm.	$17^2/_3$
0°	1.5 mm.	29	0°	0.31 mm.	$47^1/_2$
0°	0.5 mm.	$10^1/_{12}$	0°	0.21 mm.	$47^4/_5$

From this we plainly see that the velocity is greatest at 0° whilst formerly we have found a maximum velocity at — 48°. On the other hand we see once more that at — 85° the velocity is smaller than at — 48°.

6. In order to ascertain whether the presence of pink-salt exercised any influence on the position of the maximum of the velocity of change, a certain quantity from *the same* mass which originally filled the dilatometer A was introduced into a dilatometer (B) with addition of absolute alcohol but without pink-salt. The following results were obtained: —

TABLE II.

Temperature.	Velocity of change.	Time of observation in hours.
—45°	1.6	5
0°	0.0	17
—15°	0.36	6
0°	0.06	10
—85°	0.0	$3^2/_3$
—45°	0.17	$20^1/_{12}$

The maximum velocity now lies near — 45°.

From these results, taken in connection with those in Table I, it appears that the position *of the temperature at which the change proceeds most rapidly, is changed by the addition of pink-salt.*

In the experiments described previously (compare Proc. Roy. Acad. Amsterdam. 1899. 102 also Zeitschr. f. phys. Chem. 1899. 30, 616) the

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maximum was also found at — 45° in the presence of pink-salt, but at that time a tin was used which had already undergone the change of white tin $\rightleftarrows$ grey tin in both directions.

From this we see what enormous influence is exercised on these phenomena by the "*previous history*" of the white tin.

GERNEZ [1]) has noticed quite analogous phenomena with sulphur; the velocity of the change, melted sulphur → rhombic sulphur, is there dependent on T, the temperature at which the sulphur was melted, the time during which it remained fused, t the temperature at which it remained superfused, τ' the time during which it was superfused, O the temperature at which the change takes place after contact with a crystal of rhombic sulphur.

GERNEZ has published no observations showing a displacement of temperature of the maximum velocity such as has been found here. It would be of interest to investigate whether a similar phenomenon may also occur there.

7. With substances like sulphur it is not possible to do more then acknowledge the existence of these mysterious phenomena.

Now that similar phenomena are met with in a substance like tin which is electrically well-defined, there is a prospect of learning something more about these changes which are coupled with a change in free energy.

I hope soon to undertake a research in that direction.

8. In the first communication on the enantiotropy of tin [2]), it was casually remarked that the velocity of change increases when the change has occurred a few times in both directions. This is correct, but it is now evident that the transition point need not be passed, that is to say that on exposing white tin to low temperatures, the velocity of change constantly increases (at the same temperature).

The behaviour of a dilatometer [3]) which was filled with 20.370 grams of grey tin and 19.040 grams of white tin which had originated from the grey tin by warming may serve as an example.

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[1]) Journal de physique 2nd series. 1885. 349.

[2]) Proc. Roy. Acad. Amsterdam. 1899. 38.

[3]) Filled with alcohol with pink-salt. 1 mm. displacement of the liquid column in the capillary corresponds to a conversion of 10 milligrams of white tin into the grey modification.

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TABLE III.

Temperature.	Velocity of change.	Time of observation in hours.
—45°	2.33	6
0°	0.47	15 4/6
—45°	2.3	7 5/6
0°	0.7	17
—15°	3	7 1/3
0°	0.86	17 1/2
—85°	3.3	3 2/3
—45°	4.0	1 3/4

Although the active mass of the white tin has considerably decreased, the velocity at 0° has still increased from 0.47 to 0.86 that at —45° from 2.33 to 4.0.

9. From the experiments described here, it appears clearly that only those results are comparable which have been obtained with tin which has the same (preferably, known) "*previous history*".

I have, therefore, examined the curves of the velocity of change of the reaction

$$\text{grey tin} \rightleftarrows \text{white tin}$$

which in the previous communication [1]) were determined with samples having different "*previous history*", by means of one and the same sample.

TABLE IV.

Temperature.	Velocity of change.
—85°	3.3
—45°	4.0
—16°	3.0
0°	1.06
20°	— 0.09
25°	— 2.0
30°	— 20.0
35°	— 132.0
40°	—2700

It is difficult to unite these data into a clear graphical figure on a small scale and I, therefore omit this.

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[1]) Proc. Roy. Acad. Amsterdam. 1899. 103, 286.

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Summary of Results.

1. The addition of pink-salt does not only influence the velocity of the change

$$\text{grey tin} \rightleftarrows \text{white tin}$$

but also the temperature of the maximum velocity.

2. The "*previous history*" of the tin exercises a great influence on the velocity with which the above reaction takes place.

The mysterious phenomena observed by GERNEZ in the case of sulphur are also met with here. As however, we possess in tin a substance with well-defined electrical properties, there is a prospect of getting some insight, by electrical means, into the changes which this metal undergoes, since those changes must be accompanied by a change in the free energy.

3. Comparable results are only obtainable with samples having the same "*previous history*".

Amsterdam, University Chem. Lab, May 1900.

Chemistry. — "*The formation of mixed-crystals of Thallium-nitrate and Thalliumiodide*". By Dr. C. VAN EYK (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read May 26, 1900.)

1. No instance is known of the formation of mixed crystals of nitrates with iodides. Preliminary experiments showed me that a mixing in the solid state probably takes place with several nitrates and iodides. The system Thalliumnitrate—Thalliumiodide has now been closely investigated. In the first place the relation between the composition of the fused mixtures of salts and that of the mixed crystals deposited on cooling has been examined.

2. The commencement and progress of the solidification of mixtures of 100 pCt. of $Tl\,NO_3$ to 100 pCt. of Tl I was observed.

mol. % Tl I	Commencement of Solidification.	End of Solidification.
0	206°	205°.4
1.6	207°	206°
4.1	208°.6	207°
6.7	211°	208°.4

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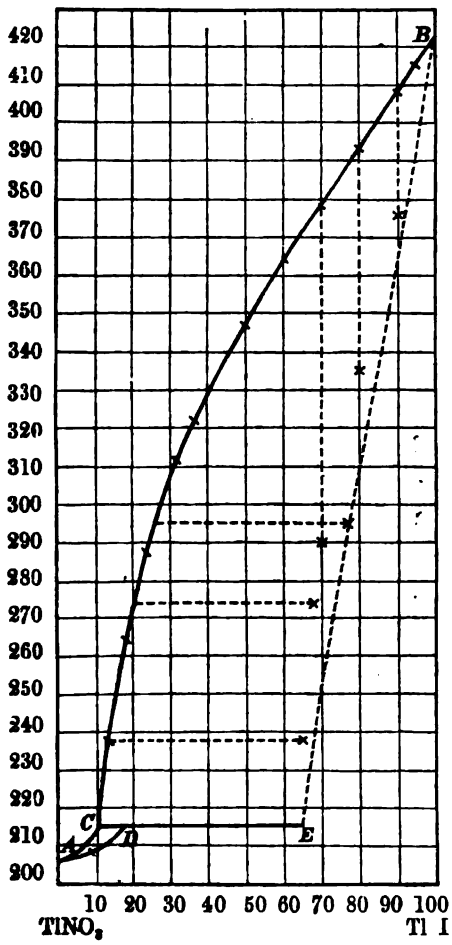
mol. % Tl I	Commencement of Solidification.	End of Solidification.
9.9	215°	209°.5
13	238°	210°
18	264°.5	215°.5
23.7	288°	»
31.4	311.°5	»
36	321°.5	»
50	346°.5	»
54.5	354°	—
60.2	363°	—
69.9	378°.5	290°
80.5	393°	335°
90.1	408°	376°
94.7	415°	—
100	422°	—

A clear view is given by the graphic representation in which the line *A C B* represents the first solidifying points. The crystals which deposit on solidification of 0 to 9.9 mol. pCt. Tl I are white, with a higher percentage of Tl I they are red.



3. From the course of the melting point line (type IV of Bakhuis Roozeboom, Zeitschr. für phys. Chem. **30**. 399), which commences to rise immediately from the solidifying point of $TlNO_3$, it follows that mixed crystals, and not the single salts, are deposited from the melt, and that the mixed crystals are of two kinds corresponding to the solidifying point lines *AC* and *CB*. This may, further, be deduced from the following: 1. the crystals which are deposited from mixtures of 0 to 9.9 mol. pCt. Tl I are white and contain Tl I, the colour of which becomes visible at lower

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temperatures on account of the change then undergone by the mixed crystals; 2. admixture of Tl I with $TlNO_3$ as well as of $TlNO_3$ with Tl I lowers the transition point of both $TlNO_3$ (142°) and Tl I (169° red ⟶ yellow).

4. The connection between the concentration of the mixed crystals and that of the melt has been determined in the case of mixtures, which begin to solidify below 300°, by isolating the crystals from the melt and subjecting them to analysis (compare Zeitschr. für phys. Chem. **30**. 432); in the case of mixtures showing a higher solidifying point it has been derived from the course of the solidification.

mol. pct. of Tl I in the melt.	mol. pct. of Tl I in the mixed crystals.
4.7	8
6.7	11.5
9.2	16.4
13.3	63
20	67
24.7	77

In this way are obtained the lines *AD* and *EB* which show the composition of the white and red mixed crystals obtained from mixtures of 0—10 and 10—100 mol. pCt. of Tl I. The second line *EB* is not so reliable as the first, as the method used for the separation of melt and crystals causes a small quantity of the melt to adhere to the drained crystals.

With melted mixtures containing more than 10 mol. pCt. of Tl I this may cause a rather large divergence in the analysis of the mixed crystals, as with these mixtures the concentrations of melt and crystals differ by more than 50 pCt.

It is, therefore, quite possible that the real values are situated a trifle more towards the right than has been found by analysis.

From the lines it follows that the white mixed crystals may contain from 0—18 mol. pCt. of Tl I and the red ones from about 65—100 pCt., so that there is here a hiatus in the series of mixtures between 18 - 65 pCt. Accordingly, all mixtures between these concentrations solidify at 215°.5 to a conglomerate of the crystals *D* and *E*.

5. Thalliumnitrate, rhombic at the ordinary temperature, is rhombohedric above 142°, whilst the yellow Thalliumiodide is described in the manuals as regular. Prof. SCHROEDER VAN DER KOLK

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had the kindness to determine the crystalline form which these salts, assume on solidifying.

The red TlI appeared to be regular, the yellow on the other hand biaxial. Thalliumnitrate also seems capable of crystallyzing from the melt in the regular system. This corresponds with the fact that the white as well as the red mixed crystals are regular.

Breda, Chem. Lab. Royal Milit. Acad.

Botanics. — "*Further researches on the Formation of Indigo from the Woad (Isatis tinctoria)*". By Prof. M. W. BEIJERINCK.

Since my first communication on the chromogene of the woad [1]) I have found that the indoxyl does not exist in it in a free condition, as I then thought, but in a loose compound which I will call isatan, and which, by an enzyme, simultaneously present, the isatase, is easily decomposed with production of indoxyl.

1. *The research of* SCHUNCK.

As soon as I had come to this conclusion, the question arose, whether the matter prepared by SCHUNCK from the woad in 1855, and described [2]) under the name of "indican", can be either or not identic with isatan. That in many of his experiments he has indeed had isatan before him I consider as certain. But in carefully reading his essay I met with number of contradictions, which are only to be explained by SCHUNCK's working with two other substances besides, which he continually interchanges with each other and with isatan; these are indoxyl and a chromogene which colours intensely yellow by alkalies, occurs abundantly in the woad, precipitates, just like isatan, with basic lead acetate, but has nothing to do with indigo. If I well understand him he calls this substance „changed indican" and considers that it differs from it by containing one or two H^2O more, but this is a wholly unproved hypothesis.

Indoxyl was not known to SCHUNCK at all, but his second preparation method of the "indican" reposes on ether extraction of the dried plant. As isatan is not soluble in ether I suppose that

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[1]) On the Formation of Indigo from the Woad (*Isatis tinctoria*). Kon. Akad. van Wetenschappen, Amsterdam; Proceedings of the Meeting of 30th September 1899.

[2]) E. SCHUNCK. On the Formation of Indigo-blue. Part I. Philosophical Magazine (4) Vol. 10, pag. 74, 1855. For the indiglucine: Ibid. Vol. 15, pag. 127, 1858.

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during the preparation small quantities of indoxyl originated from the isatan, which easily occurs under various influences, and for which ether is an excellent solvent.

However strange it may be, it was the matter colouring yellow by alkalies, and not the indigo-chromogene itself, which SCHUNCK subjected to the three analyses on which reposes the well-known formula of the "woad-indican". Quite clear he is not, but so far as I conceive his meaning, the first and the third preparations, which he analyzed, contain no indican at all, yet he calls them the purest; the second he considers as less pure, and he seems to have subjected it to the analysis after having convinced himself that by precipitating it with alcohol, lead acetate and ammonia "it contained no longer unchanged indican", which consequently means, that he had before him the said matter turning yellow by alkalies and thus containing no more indigo chromogene.

Word for word he says the following, first concerning his analyses in general (l. c. Part I, pag. 89): "I have hitherto been unable, I regret to say, to ascertain the exact composition of indican by direct experiment. On account of the deliquescent nature, and its so readily undergoing change when heated, it was impossible to subject it to analysis in a free state and I was therefore obliged to have recourse to the lead-compound." Then follows the description of the three analyses themselves. Of the first he says (l. c. pag. 90): "Notwithstanding the care, however, which I took in the preparation of the specimen, I found that it did not contain unchanged indican, as a little of it, when tested with sulphuric acid, gave no indigo-blue. It is nevertheless the purest specimen of the lead-compound which I have analysed". Then he says of the second and third: "The next analysis which I shall give, places in a striking light the effect which alkalies exert on indican. I took some of the same solution of indican which I had employed for the preceding analysis, and which I found to give, when a little of it was boiled with acid, very pure indigo-blue; but instead of evaporating it, I added a large quantity of alcohol to it, and then precipitated with acetate of lead and ammonia. The precipitate no longer contained unchanged indican"... "The third analysis was performed with a lead-compound made in the same way as that of the first analysis." [1])

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[1]) Three analyses of such doubtful substances are the sole foundation upon which the well-known indican formula of SCHUNCK

$$C^{26}H^{31}NO^{17} + 2\,H^2O = C^8H^5NO + 3\,(C^6H^{10}O^6).$$

Indican — Indigo-blue — Indiglucine

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All this is not quite clear, but I read from it that these analyses have nothing to do with the indigo chromogene itself, that is to say, with isatan, and I think that they relate to a mixture of the chromogene from the woad, which colours yellow by alkalies, and plant-slime ("indiglucine"). The explanation of this enormous fact should, I think, be sought in the following circumstances. SCHUNCK prepared the "indican" by alcohol extraction from carefully dried woad-leaves, which in itself is quite rational, because in this way relatively concentrated and rather pure solutions are obtained. But if the dried leaves are kept a little too long, for instance two days at 26° to 30° C., or if they grow a little moisty, the isatan vanishes completely from them. Though SCHUNCK evidently knew that the chromogene can easily disappear from the dry leaves, he does not mention the short time after which this occurs already, so that I think it very well possible that the chromogene has disappeared during his preparation without his having observed it. For it is to be kept in view that his method of demonstrating the indigo-blue qualitatively is highly deficient and consisted in decomposing the chromogene by "strong mineral acids", the very worst method to be followed, as strong acids are pernicious as well to isatan as to indoxyl.

My opinion that SCHUNCK at the moments when it was particularly important, had not to do with the indigo chromogene itself, but with another substance, is also based on several observations which he makes about the properties of the "pure indican". So we read on pag. 85 (l.c. Part I): "With caustic alkalies, baryta and lime-water the watery solution turns of a bright yellow." This reaction holds only good for the impurity which remains in the dried leaves after the isatan is destroyed in them. If in the preparations any isatan had been present the yellow colouring would have been immediately followed by the formation of indigo-blue, which then becomes much more distinctly visible than if the same preparation is decomposed by acids. Evidently he has examined different samples with acids and alkalies, and samples, free from isatan, only with the latter, else he would certainly have found that those preparations, which by acids produce indigo-blue, yield much more indigo if they are treated with an

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is based and which, since 1855, has been accepted, without criticism, in all great chemical manuals. Formerly I was inclined to write the formula thus:

$$C^{26}H^{27}NO^{17} + 2\,H^2O = C^8H^7NO + 3\,(C^6H^8O^6)$$
Indoxyl Glukoron

but now, having carefully studied SCHUNCK's essay, I think this interpretation also worthless.

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alkali. Likewise the following statement of his preliminary researches is for the greater part unintelligible if it is admitted that SCHUNCK speaks of isatan. He says (l. c. pag. 81): "I was enabled to infer, with positive certainty, that the *Isatis tinctoria* contains a substance easily soluble in heat and cold water, alcohol and ether, which, by the action of strong mineral acids, yields indigo-blue; that the formation of the colouring matter from it can be effected without the intervention of oxygen or of alkalies; and that the latter, indeed, if allowed to act on it before the application of acid, entirely prevent the formation of colouring matter." In opposition to this, the fact must be stated, that the best method for demonstrating with certainty and quickness isatan or indoxyl in woad-sap, just consists in adding alkali to it, by which the isatan is decomposed and the indoxyl is quickly oxidized to indigo at the air; after this, the addition of acid may be desirable to decolour the yellow pigment formed by the alkali, by which the indigo-blue appears with greater purity.

The uncertainty of the whole research explains how it is possible, that SCHUNCK, when later becoming acquainted [1]) with *Polygonum tinctorium*, could think that the indican therein occurring, the composition of which, $C^{14} H^{17} NO^6 + 3 H^2 O$, has recently been determined by Messrs. HOOGEWERFF and TER MEULEN [2]), and which is entirely different from isatan, could be identic with his „woad-indican."

Consequently I believe that SCHUNCK cannot be considered as the discoverer of the isatan, though it is not to be doubted, that in his experiments, he has sometimes had this substance before him, and, basing on the above exposition I take his indican formula for not appliable to isatan.

2. *Preparation and properties of isatan.*

Indoxyl and isatan are very unstable and still at present most imperfectly known substances, which only in acid solutions can easily be distinguished from each other, in neutral solutions, without the use of isatase, with much more trouble, in alkaline solutions not at all, because in these isatan produces indoxyl.

The reason why at first I thought that the woad must contain free indoxyl and no compound of it, is the fact that in the extracts obtained

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[1]) On Indigo-blue from *Polygonum tinctorium*. The Chemical News. Vol. 39, pag. 119, 1879.

[2]) Kon. Akad. van Wetensch. te Amsterdam, 31 Maart 1900, pag. 598.

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from young woad-leaves, rich in isatan, as well by decoction as by cold extraction, the isatan is decomposed and an indoxyl solution is obtained. Now I admitted in the beginning, that if in the woad, as was my leading theory, a glucoside was present, which, in analogy to the indican, must be decomposed by an enzyme, at the decoction no indoxyl but exclusively this glucoside would be obtained, because by boiling the enzyme is suddenly destroyed. In this view I was supported by the fact, that this indeed takes place with *Indigofera* and *Polygonum*, which by decoction yield indican, by cold extraction indoxyl.

But I began to doubt of the generality of this theory, when observing, that *Phajus grandiflorus*, which belongs to the indican plants, nevertheless [1]) produces indoxyl at decoction. So this seemed also possible with the woad, though it was clear that the properties of the „glucoside" ought in this case to be quite different from those of indican.

But I was only put on the right way, by the experience, that it is possible to obtain from the leaves of the woad, by the extraction with dilute acids a solution, which remains unchanged at the air, although it yields with alkalies much indigo-blue, while an equally acid indoxyl solution slowly oxidizes at the air to indigo. I then clearly saw why I had before obtained indoxyl from the woad. My experiments had been performed on a small scale; I had been able with care to select growing leaves and buds only; but they contain much isatan and so little acid, that the enzyme isatase can become active, so that by decoction, as well as by cold extraction with water, and even with alcohol, they produce indoxyl, though at the decoction and alcohol extraction mixed with much isatan, which fact I only observed later. If I had used older leaves which contain more acid, I should have found at once isatan quite free from indoxyl.

The relative constancy of isatan in feebly acid solutions, even at boiling temperature, can be utilized for its preparation.

Though the acidity during the extracting must be feeble yet it must be strong enough to prevent the decomposition of the isatan by the isatase. To this end an acidity of 1.6 to 3.2 cc. of normal oxalic acid per 100 cc. of the extraction liquid, (0.1 to 0.2 weight percentage) suffices, for the acidity of the older leaves themselves amounts to about 1,5 cc. normal per 100 cc. of the juice, and this is the very limit of acidity above which the isatan becomes inactive. If the extraction is effected by boiling, this degree of acidity should be

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[1]) Indigofermentation. Kon. Akad. van Wetensch. Amsterdam, Proceedings of the Meeting of Mar 1900 pag. 573.

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exactly observed. In cold extraction, with oxalic acid, the isatan is much less subject to decomposition, so that, below 50° C. solutions of 1 to 3 pCt. oxalic acid can safely be employed. But at these low temperatures the acid penetrates with less rapidity into the cells, in which accordingly the enzyme can become more or less active producing some indoxyl. Hence, in the acid extraction at low temperature, it is advisable to rub the leaves down in a mortar, immersed in the acid liquid.

In particular at boiling temperature and when using an extraction liquid of an acidity of 2 to 3 cc. of normal oxalic acid, it is easy to obtain a quite undecomposed isatan solution from the growing woad-leaves, even of the youngest still neutrally reacting meristemes. In consequence of the boiling temperature, aided by the perfect surrounding of the cells with the dilute acid, the isatase is destroyed simultaneously with the dying of the protoplasm, by which decomposition of isatan is quite excluded. As the extraction continues, there is an interchange between the feabler acidity within (0.5 cc. normal pCt.), and the stronger acidity without the young cell, and at the end of the experiment, a solution of isatan of 0.5 to 2 cc. of normal acid per 100 cc. of juice in obtained, when the weight of the leaves used, equals that of the extraction liquid.

More acid used in the boiling than the said percentage causes isatan decomposition, by which not only indoxyl but also brown products of decomposition originate.

Oxalic acid can be replaced by other acids and by acid salts. Thus I obtained good results with dilute sulphuric acid and phosphoric acid, and with a saturated solution of boric acid, at room temperature. Acetic acid causes a feebler decomposition than oxalic acid. When the appearance of brown products of decomposition during the boiling is taken as a criterion for the decomposition, I found that 12 cc. of normal acetic acid added to 100 cc. of juice (ca 0.8 weight percentage), is about proportioned to 5 cc. of normal oxalic acid (= 0.3 weight percentage). Acid salts act like acids. Kaliumbioxalate and biphosphate can only be used in strongly diluted solutions. With a cold saturated solution of kalium bitartrate the extracting may be operated at boiling temperature without decomposition; only by prolonged boiling a little indigo-blue is produced. I prefer, however, the extraction with oxalic acid. Therewith the solutions remain clear and of a light yellow and can very easily be filtered [1]); after filtering, the remaining leaf-matter is soft, but

[1]) If the woad-leaves are boiled with more acid than 2 to 3 cc. normal per 100 cc. of the juice, the decoction grows slimy and gives trouble in filtering.

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by no means slimy, and can quite well be pressed dry, so that, in consequence of the high water percentage of the leaves, a quantity of extract is obtained nearly twice as much as the original volume of the oxalic-acid solution.

If with the thus obtained isatan solution enzyme experiments are to be performed, the acid must be removed, which is best done by boiling with chalk [1]). As the reaction of the chalk is slightly alkaline it should be very finely divided, as larger particles form a little indigo on their surface. After filtering off the oxalate and the superfluous chalk, a liquid results, somewhat brownish indeed, but not so much as to be hurtful to the enzyme experiments.

This liquid cannot be evaporated to dryness without being decomposed, even not at room temperature, because during the concentration the acidity increases. To neutralize the syrupic matter is troublesome.

The extraction of the isatan can also be effected with feebly acid alcohol, both in the cold and at boiling temperature. Fresh leaves are then to be preferred to dried ones, because in drying there always gets lost some, at last all isatan. The alcohol extract must be evaporated at low temperature and finally be neutralized with chalk. After boiling a brownish, almost neutral and very rich isatan solution is obtained, which can be purified with neutral lead acetate.

For further concentration the isatan can be precipitated with basic lead acetate, and the yellow precipitate be decomposed in the cold with oxalic acid. The lead oxalate separates freely from the isatan solution, and the excess of oxalic acid can be removed with chalk, the lead with sulphurated hydrogen. This solution can be kept without decomposition for some time, but after a few weeks the isatan vanishes.

In the decoction method with oxalic acid, followed by lead precipitation, the chlorophyll is removed from the very first and evaporation is excluded. More plant slime will then precipitate with the lead than by alcohol extraction, but on further purifying, this slime can be precipitated with ether-alcohol. I have as yet not been able to prepare dry isatan, as a powder, from these extracts, such as I before prepared the indican.

The most characteristic difference between indican and isatan consists in their behaviour to alkalies: indican is constant in concentrated alkaline solutions, isatan is decomposed by very feeble alkalies, even

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[1]) Neutralizing without endangering the subsequent enzyme action, can also be done with lead-, mangan-, magnesia-, or baryta-carbonate, but I prefer chalk.

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in the cold. Concentrated solutions of dinatrium phosphate, phosphoric salt and ammonium carbonate produce indoxyl from isatan, already at room temperature. By acids, both indican and isatan are decomposed, but indican with much more difficulty, which is especially evident when using acid salts. So, isatan is already decomposed by boiling with dilute kalium bioxalate, in which indican is constant.

Both substances precipitate with basic lead acetate, producing yellow precipitates, which colour is probably proper to the substances themselves, and not to impurities.

Isatase, the specific enzyme from woad, does not act on indican; isatan on the other hand is not decomposed by the indigo-enzymes.

Isatan is not directly splitted by the common microbes; indirectly it may, of course, be decomposed by the alkali produced by microbes. Indican, on the other hand, as I have formerly shown, is directly decomposed by many microbes, either by ferment action of the protoplasm (katabolism), or by specific enzymes, proper to the microbes. This difference between isatan and indican is probably related to the nature of the substances set free in the decomposition beside the indoxyl. So the glucose, from the indican, is an excellent nutrient for many bacteria, whilst the very stability of the isatan in relation to microbes, seems to indicate that the matter, which besides indoxyl originates from it, is no glucose, perhaps no sugar at all.

3. *The isatase.*

The preparation of the woad-enzyme is effected in the same way as that of the indigo-enzymes. The related parts of the plant are rubbed down in living state under alcohol, and the alcohol is so often renewed until all the chlorophyll pigment is removed. After filtering and drying the crude isatase is obtained as a white, feebly acid powder in which, of course, all substances not soluble in alcohol are present, hence, all the other enzymes of the woad too. As the enzyme is quite insoluble in water it can be purified by extraction with destilled water, by which the other enzymes, at least those that are soluble, disappear. Solvents for the isatase itself I have not yet found.

As the woad, like the cabbages, is very rich in gypsum, the crude isatase contains so much of it that to remove it with destilled water is troublesome. I have therefore, in order to answer the question, whether in the action of isatase on isatan perhaps a sulphate is produced, as in the splitting of kalium myronate by

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myrosine, prepared in the following way isatase free from gypsum. Woad leaves cut fine were rubbed down in destilled water, then pressed out, and the remaining matter extracted with water until the filtrate proved free from sulphuric acid. Then the chlorophyll pigment was removed by alcohol and the remaining matter dried and powdered.

Though the thus obtained preparation is poor in enzyme, because this is localized in the chlorophyll granules, which during the pressing of the leaves are for the greater part also pressed out, it is still sufficient to bring about a strong isatan decomposition. As was to be expected, sulphates were not thereby set free.

The isatase is spread through the whole woad-plant; it occurs as well in the growing parts as in full-grown roots, stems, leaves, and flowers. So the distribution is another than that of the isatan, which is wanting in all full-grown parts, and is the more accumulated in growing roots, stems, and leaves, the younger they are. Another distribution also than that of the indigo-enzymes in the indican plants, which are only found in the parts rich in indican.

On the other hand the distribution of the isatase within the cell itself, corresponds with that of the indigo-enzymes: both are localized in the chromatophores. The isatan has also, in the cell, a localisation corresponding with that of the indican, for in as much as can be inferred from micro-chemical experiments, both are found in the living protoplasm of epidermis, mesophyll and other parenchymatous tissues. For establishing the localisation of isatan and isatase in the cell, the same way can be followed which I formerly pointed out for detecting the indican and the indigo enzymes [1]).

As regards the isatan, for this end, not too thin microscopic sections of young, vigorously growing stems or leaves are put in a boiling mixture of hydrochloric acid and isatine; by the acid indoxyl is separated, which produces, with the isatine, red crystal needles of indigo-red, localized in the protoplasm. More difficult to observe, but still, I think, quite convincing is the precipitation of indigo-blue, as small granules, in the living protoplasm, when the sections, in a living state, are put in a mixture of boiling hydrochloric acid and ferrichlorid. Remarkable is the strong accumulation of isatan in the epidermis cells, and especially in the hairs found on the young leaves.

The localisation of isatase in the chromatophores can be demonstrated in two ways. Either little bits of the easily loosening epidermis of woad-leaves, or microscopic sections of stems or leaves, all in a

[1]) Indigofermentation p. 579.

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living state, can be put in a neutrally reacting woad-decoction, rich in isatan, and heated to ca. 45° C. After some minutes already the chromatophores begin to colour blue; the intensity of colour increases some time, to reach its limit in an hour or so.

The blue-colouring of the colourless chromatophores of epidermis and stem-pith, is here distinctly to be observed, so that, particularly the fragments of the first, become very interesting preparations.

The localisation of the isatan in the protoplasm, of the isatase in the chromatophores, renders their inter-action in the living cell possible without any influence of the acid cell-sap. At the death of the cell, this state will suddenly change and the acidity of the cell-sap determines whether the isatase can act or not on the isatan.

In no other plant but the woad I have hitherto been able to detect isatase. I had expected its presence in some short-valved Cruciferae. So in *Capsella bursa pastoris*, where, in case the root-neck is much hurt, a trace of indoxyl can be pointed out, but here also the enzyme is wanting. Likewise it wants in the indican plants. Also all microbes examined are devoid of isatase.

4. *Action of isatase on isatan.*

The action of isatase on isatan is, as observed before, only possible in neutral or amphoteric and very feebly acid solutions. In alkaline solutions the observation becomes uncertain, because the alkali itself splits off indoxyl. If the acidity amounts to 1.5 cc. of normal acid per 100 cc. of the isatan solution, the action is much weakened, and at ca. 1.8 cc. of normal acid, there is no more decomposition of isatan at all, which is noteworthy as this percentage of acidity is reached in the cell-sap of older woad-leaves. This does not however exclude isatan-decomposition by the enzyme in the living cell, as the process can be limited to the protoplasm, in accordance with the localisation described.

As the action of the isatan is judged after the formation of indigo-blue, two chemical processes are involved in it, isatan-splitting and indoxyl-oxidation. If the experiment is performed with free access of air, for instance in a thin layer of the isatan solution, with the enzyme floating on it, the indoxyl changes directly into indigo; but if the isatan is decomposed with imperfect access of air, for instance, in the depth of an experiment tube, then it is necessary, during the experiment itself, to render the oxidation of the indoxyl as complete as possible by agitation with air, which does not however always succeed with sufficient quickness, and so limits

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the accuracy of the experiment. Of course the liquid cannot be alkalized, because then not only the indoxyl formed by the isatase would become visible, but also the indoxyl set free by the alkali from the isatan not decomposed by the isatase. If the object is to observe the isatase action at a determined temperature, then the enzyme cannot be destroyed at the end of the experiment by heating, but this must be effected by some enzyme poison, as for instance sublimate.

Addition of acid to render the colour of the indigo-blue more pure must likewise be avoided, in order not to decompose isatan.

Accordingly it is necessary to perform the reaction in a very feebly acid solution, and to judge of the results without other precautions than a thorough aeration. I have not been able hitherto to answer the question after the nature of the matter, which at the isatan-splitting, most probably is set free beside the indoxyl. Pressed yeast, produces in woad-extract, heated with crude isatase at 30° C., more alcohol and carbonic acid, than in the same extract without isatase (in the proportion of 8 : 5), so that in the first there must certainly be formation of sugar capable of fermentation. But this sugar results, probably not from the isatan, but from the action of other enzymes, present in the crude isatase, on glucosides or carbohydrates, present in the isatan-solution, such as myrosine on myronates, and diastase on granulose.

The process of the decomposition cannot be studied with FEHLING's cupric solution, as the isatan is decomposed by the alkali.

That to SCHUNCK's "indiglucine" no value can be attached follows from § 1.

In order to state the influence of heating on the isatase action, the experiments were arranged as described elsewhere for the indigo-enzymes [1]), with the difference, that for the above reasons, alkalisation and subsequent acidification are here omitted. The very finely powdered enzyme is shaken in an experiment tube with the isatan solution, and in a water bath, at determined temperature, heated a determined number of minutes. There are always performed two experiments at the same time, so that a colorimetrical comparison of the produced indigo is possible, e.g. at 48° C. and 50° C., or at 40° and 60°, 45° and 55°, etc. The best results were obtained with dilute isatan-solutions, which are brought, as exactly as possible, to an acidity of 0.5 cc. normal per 100 cc. of liquid, and with so little enzyme, that the complete conversion was very slowly accomplished and took about half an hour.

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[1]) Indigofermentation pag. 586.

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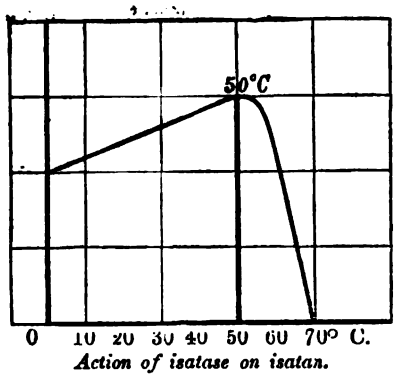

Action of isatase on isatan.

The optimum for the action was found at 48° to 50° C., but could not be determined more accurately as differences of two 2° C. produce no distinct colorimetrical difference. At 70° C. the enzyme is completely destroyed. The minimumlimit is low, far below 0° C., as is seen in the figure. Noteworthy is the slowness with which the intensity of action decreases at decrease of temperature, and the quickness with which it takes place when the temperature rises. So the action at 10° and at 0° C. respectively is as strong as at 60° and 60.5° C.

On other substances but isatan isatase seems not to act; it has certainly no action on indican, neither could I decompose with isatase the potassium indoxyl-sulphate in horse urine.

When judging of these experiments it must be kept in view that other enzymes are present in the crude isatase, which may produce substances not indifferent for the isatase action. So, mention was made above of the presence of myrosine and diastase in the crude isatase preparations, and below I will refer to the presence of peroxydase.

5. *Extraction of indoxyl from the woad-leaves.*

Once acquainted with the chief properties of isatase and isatan, it is possible at will to extract isatan or indoxyl from the woad. Though in my former communication I spoke already of the indoxyl extraction, my being unacquainted with isatase prevented me from doing this with perfect clearness.

As alkalies produce indoxyl from isatan the extraction of woad-leaves therewith will at every temperature produce indoxyl. But by the presence of alkalies the indoxyl becomes so very oxidisable and then passes at the air so quickly into indigo, that the air, ever present in the leaves, causes a great portion of the indoxyl to get lost. On the other hand, neutral, or feebly acid solutions oxidize much more slowly; it is true that also in these finally all the indoxyl passes into indigo, but such solutions keep unchanged for hours at room temperature and are fit for studying the properties of the indoxyl.

The chief point for obtaining such neutral or feebly acid indoxyl solutions from woad-leaves, is during the extraction to further the isatase-action, consequently to do the very thing which I formerly

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indicated as essential for the indoxyl extraction from indican plants, where all depends on the action of the indigo-enzymes. With woad this can best be effected by keeping the extraction temperature between 45° and 50° C, and by addition of chalk or of a salt of feebly alkaline reaction, partly to neutralize the acid of the leaves. Thus a good result is obtained by entirely filling a wide-mouthed stoppered bottle with young woad-leaves, and pouring over them a $^1/_2$ pCt. dinatrium-phosphate solution ($Na^2 H PO^4 + 12 H^2 O$), heated at about 50° C., removing the air as much as possible, closing the bottle and allow it to stand at 40° C. for 24 hours. By decantation and pressing the leaf matter, boiling and filtering, all the indoxyl is obtained in an amphoteric solution, which is somewhat brownish, but is excellent for indoxyl experiments. The presence or absence of undecomposed isatan is observed by precipitation with lead acetate, whereby the indoxyl remains dissolved. The indoxyl can also be shaken out with ether and in the remaining liquid sought with isatase for isatan. Not decomposed isatan remains also in the filtrate, when the indoxyl is allowed to oxidize at the air and the indigo-blue is filtered off.

The ether solution of the indoxyl, obtained by shaking it out of the extract, can be evaporated at low temperature at the air, by which the indoxyl is left behind as a liquid soluble in water, which can be coloured by different impurities. Though the watery solution of this "purified indoxyl" is inconstant at the air, its oxidation to indigo-blue proceeds slowly enough for studying the influence which different substances exert on this process.

Various circumstances have induced me to put anew the question, whether in this oxidation an oxidizing enzyme is active [1]). After much doubt I have finally, as before, come to the conclusion that such is not the case. My primitive uncertainty was caused by the very unequal acceleration of the oxidation of indoxyl solutions by different powders spread on the surface. So the oxidation is somewhat furthered by the crude enzyme of woad, and very strongly, by that of *Indigofera leptostachya*, but by boiling, the crude enzymes are by no means deprived of this property. By a minute comparison of the behaviour of crude indoxyl solutions prepared from isatan and indican, with "purified" ones [2]), I ascertained

[1]) Mr. BRÉAUDAT erroneously asserts (Compt. rendus T. 127, p. 769, 1898 and T. 128, p. 1478, 1898) that in the extracts of *Isatis* indigo-white occurs, which, by an oxydase is turned into indigo-blue.

[2]) Besides from woad I prepared indoxyl by decomposing in a closed bottle a 4 pCt. indican solution with indigo enzyme at 60° C. Moreover Mr. H. TER MEULEN had the kindness to prepare for me in the Chemical Laboratory of the Polytechnical School indoxyl solutions in chemical way. The "purified" indoxyl was always obtained by ether extraction.

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that, both in the crude enzymes and in the crude indoxyl solutions, there are present soluble and insoluble chemical compounds, which influence the quickness of the indoxyl oxidation, but which are not destroyed by enzyme poisons and by heating, and which accordingly have not the nature of enzymes.

Crude isatase has neither an oxidizing action on pyrogallol, hydrochinon, and guajac emulsion.

Though thus oxydase is wanting in the crude isatase, there is present in it, as in all such like powders, prepared at random from higher plants, peroxydase ("leptomine" of RACIBORSKI) [1]), that is the enzyme which, in the presence of hydrogen peroxyd, colours guajac emulsion blue. But indoxyl is by no means oxidized by it to indigo.

6. *Nekrosis and Nekrobiosis.*

Living tissues can die off in two ways: by necrosis, that is the dying of the protoplasm with simultaneous destruction of the enzymes, and by necrobiosis, in which the protoplasm dies, but the enzymes remain active. The phenomenon, formerly described by me as the "blue stripe" in partly killed woad-leaves, on the confine of the living and the dead portions, which both retain their green colour, reposes accordingly on necrobiosis. The action of isatase on isatan explains this phenomenon satisfactorily and renders my former hypothesis of alkali formation at the dying of the protoplasm superfluous.

The simplest way to perform the experiment is to kill the tip of a young woad-leaf in a BUNSEN flame, or in the vapour of boiling water, then to allow the leaf to remain at ordinary temperature, by which in the said part alone indigo precipitates. If the chlorophyll pigment is extracted with alcohol, then both the "living" and the "dead" parts become colourless, the portion between them blue. The phenomenon is best distinguished in young woad-leaves; in older leaves, with a higher acid percentage, it is hardly to be observed because the acid renders the isatase inactive.

In various other plants, too, nekrobiosis causes formation of pigments. If these pigments are brown or black, and if the experiment is performed in the usual way with the leaves of these plants, then the coloured stripe may become still much more marked than in the woad. Particularly fit for this demonstration are the leaves of *Pyrus communis*, *Trollius*, *Aconitum*, *Asarum.*, *Salix purpurea*, *Populus nigra* and several other species, which at necrobiosis turn of a jet

[1]) Berichte der Deutsch. Botan. Gesellschaft. Bd. 16, pag. 52, 119, 1898.

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black and at necrosis remain green. Pear-leaves especially are recommendable for the experiment; the enzyme in them is tyrosinase, the nature of the chromogene is unknown, tyrosine it is not. Hence, when preparing a herbarium, the chief thing to keep such plants uncoloured, is to prevent necrobiosis. This frequently happens of itself, as the acid cellsap is so much concentrated in drying, that enzyme action cannot occur; so in the drying of woad-leaves, where the highly sensitive isatase remains inactive. In other cases, to obtain this end, it will be necessary to destroy the enzyme, either by boiling water, or by poisonous vapours.

Sometimes necrobiosis gives rise to aromatic or stimulant matters, which are present in the plant itself as glucosides, from which they are set free by specific enzymes at the dying of the cells. This fact is well-known regarding the myronates and the myrosine of the Cruciferae, the amygdaline and emulsine of the Amygdaleae, the spiraeine, gaultherine and gaultherase of *Spiraea*. But it holds good, too, for the cumarine of *Asperula odorata*, which appears not in it as such, but as a glucoside, which by necrosis continues unchanged and hence can be removed from the plant by boiling, while there is besides in this plant a specific enzyme, which by necrobiosis produces from the glucoside cumarine. This enzyme is not identic with emulsine and differs likewise from gaultherase. In a quite corresponding way the aromas originate from the fruit of the vanilla and the roots of *Geum urbanum*.

The comparative study of necrosis and necrobiosis in plants shows the way for the detection of a number of new chromogenes or glucosides and specific enzymes.

Conclusions.

Indoxyl occurs not, as I formerly thought, in a free state in the woad but as a loose compound, called by me isatan.

Isatan is only constant in feebly acid solutions, and is obtained by extracting the woad therewith. It is decomposed, under formation of indoxyl, by alkalies and stronger acids, and in solutions, less acid than 1.5 cc. of normal acid per 100 cc., by an enzyme, isatase, which acts the most vigorously at 50° C., and occurs in all parts of the woad-plant.

Isatan is not decomposed by the indigo-enzymes nor by microbes in as much as the latter do not form alkali. Isatase does not act on indican.

Isatase is localized in the chromatophores, isatan in the protoplasm,

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which is in accordance with the formerly described localisation of the indigo-enzymes and of indican.

If woad is extracted without acid, so that the isatase can act, or with dilute alkalies, e.g. $^1/_2$ pCt. solution of dinatrium phosphate, indoxyl is produced.

The necrobiotic stripe in partly killed woad-leaves results from the action of isatase on isatan.

Geology. — "*The Amount of the Circulation of the Carbonate of Lime and the Age of the Earth*". II. By Prof. EUG. DUBOIS. (Communicated by Prof. J. M. VAN BEMMELEN.)

In my first communication on this subject I have quoted a number of reliable data from which it follows that the waters of those rivers in whose drainage areas much limestone occurs, as is mostly the case with the larger rivers, are more than saturated with carbonate of lime, when reaching the ocean.

In consequence of their being polluted, to an extraordinary high degree, with organic matter, the quantity of carbonate of lime in the waters of many rivers of that kind, whose drainage areas are very thickly populated, in Europe and partly too in other parts of the world, is larger than in the primitive condition, before man existed in large number, thus during almost the whole past of the earth. In this respect I draw attention to the relatively higher quantity of carbonate of lime in such rivers as the Thames and the Seine, and also of the difference in that quantity between small and large rivers and lakes, as well as of some other facts showing the influence of the pollution of the water by organic matter on the relative quantity of dissolved carbonate of lime. The drainage water of soils, rich in humus, holds, for instance, considerably more carbonate of lime in solution than would correspond with saturation under the only influence of the atmospheric carbonic acid. But down the course of the rivers the last influence becomes by far the more preponderant.

Taking into consideration that in general the quantity of carbonic acid, produced by the decomposition of organic matter, increases somewhat at the mouths of the rivers, where much of that matter settles, and starting from the existing analyses, it seems to me that an average quantity of 95 mgrms. carbonate of lime per litre of water would represent, on the whole, with approximative accuracy, the primitive condition at the mouths of those rivers which have been so largely in contact with limestone that their waters could be saturated with carbonate of lime.

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This ample contact of flowing waters with limestone seems to exist in almost every case, where true sedimentary formations predominate in their drainage area. Where, on the contrary, crystalline silicate rocks prevail in the drainage area, the quantity of carbonate of lime in solution decreases in the river-waters to a more or less lower amount.

According to the analyses by Kyle, quoted in my first paper, the Rio de la Plata keeps, 8 KM. above Buenos-Aires, per litre of water only 23 mgrms. carbonate of lime in solution. The drainage area of this large river consists for the larger part, by the side of Pampas-formation, of sandstones, Archean crystalline rocks and only little Palaeozoic rocks. The Amazonas, which, between the narrows and Santarem, keeps, according to the quoted analysis by Frankland, 27.5 and at Obidos, somewhat up the river, according to two other analyses, by Katzer, 11.4 to 14.6 mgrms. carbonate of lime in solution per litre of water [1]), drains principally regions of gneiss, sandstones and clays. The same is the case with the Rio Pará (Tocantins), which, according to the analysis of a sample of the water from the harbour of Pará, taken during very low tide, keeps in solution 12.4 mgrms. carbonate of lime per litre of water [1]).

The waters of most of the rivers and river-lakes mentioned in this and in my first communication, as examples of the kind keeping fewer dissolved carbonate of lime in solution than the quantity corresponding to saturation, have, however, not been exclusively in contact with silicate rocks, but also with some limestone.

The waters of some other, mostly small, river-lakes on the contrary, have not been in contact with limestone and derive the calcium carbonate they keep in solution entirely from the decomposition of silicate rocks or the desintegration products of silicate rocks. Such are those from the Lake of Starnberg, with 4.8 mgrms., Loch Katrine, with even much less than 4.8 mgrms., Reindeer Lake, with only a slight trace, and the Rachel-See, with 2.22 mgrms. calcium carbonate per litre of water; further the five named small French lakes with outlet, surrounded by granite and basalt, having a mean quantity of 8.9 mgrms. calcium carbonate in solution per litre of water.

For a comparison of the relative quantity of calcium carbonate in the five latter small river-lakes, draining regions of silicate rocks, with that of five equally small French river-lakes, in whose drainage

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1) F. KATZER, Das Wasser des unteren Amazonas. Sitzungsberichte der Kön. Böhmischen Gesellsch. d. Wissensch. Math. naturw. Classe. Jahrg. 1897. Prag 1898, N° XVII, p. 3—6 and 8.

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areas limestone abounds, and which are likewise situated on a high level, I have dressed the subjoined table [1]).

Lakes of	Height above sea-level, in M.	Volume, in millions of M^3.	$CaCO_3$, in mgrms. per litre.
Issarlès	997	60.0	10.0
Pavin	1197	23.0	15.7
Gérardmer [2])	660	19.5	7.5
Chauvet	1166	17.3	6.5
Godivelle-d'en-Haut	1225	2.7	5.0
		Mean	8.9
Paladru	501	97.2	150.9
Chalain	500	46.6	136.4
Nantua	475	40.1	155.5
Remoray	851	12.1	182.0
Sylans	584	4.8	152.6
		Mean	155.5

The mean relative quantity of $CaCO_3$ in solution in the latter group is 17.5 times as high as that of the first group of river-lakes.

Concerning the waters of the rivers and river-lakes, which have a higher relative quantity of calcium carbonate than those of the just mentioned lakes in granite and basalt, we can trace in most cases that, although they flow over crystalline rocks, they also have had an opportunity to dissolve some calcite.

So in the cases of the Rio de la Plata, which contains 23 and the Amazonas, which contains 11.4 to 27.5, of the Rio Pará, which keeps 12 4 mgrms. $CaCO_3$ in solution per litre of water, of the Dwina with 20.2, the Delaware with 25, the Croton River with 28.5, the Ottawa with 24.8, the Moldau with 19.4, the Uruguay with 16.2, Lake Superior with 30.8, Lake Tahoe with 23.2, Lake Baikal with 40.1 mgrms. $CaCO_3$ in solution per litre of water. The Hudson River, with 42 mgrms., is moreover connected through

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1) The figures here quoted are also taken or calculated from the statements in DELEBEQUE's Lacs français. The reader will have noticed, that in the small table on p. 8 (51) of my first communication the volumes should be in *millions* of M^3.

2) The quantity of $CaCO_3$ given here, which is also taken from DELEBEQUE's Lacs français, concerns the water of the surface, the formerly given the bottom water.

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a channel with Lake Ontario, which is rich in dissolved carbonate of lime. For Lake Tschaldyr there is not sufficient information available to judge whether we have to think of the same mixtion with dissolved $CaCO_3$ or that the relatively high quantity of this matter is indeed to be interpreted by a particularly quick decomposition of silicates, as supposed in my first paper.

From all the available data it is evident that the quantity of calcium carbonate in solution in river waters is determined by the nature of the rocks with which they have been in contact. Indeed a great contrast is to be observed between the waters containing only the lixiviation products of crystalline silicate rocks and those flowing to some extent over true sedimentary formations. In the latter case the contact of the waters with limestone proves almost always sufficient to bring about a saturated solution of calcium carbonates.

If we estimate that in regions consisting entirely of crystalline silicate rocks — all other circumstances being equal — on an average *a tenth part* carbonate of lime is annually carried in solution by the flowing waters as in regions where limestone abounds, this estimate certainly remains rather below the real proportion.

Assuming moreover that the regions of the earth consisting of crystalline silicate rocks are on the whole in contact with as much flowing water as those where only true sedimentary formations are found — an assumption we may make with safety, as appears from the comparison of pluvial with geological maps — and taking, further, according to the figures given by Tillo, that the crystalline silicate rocks cover the fourth part of the land area of the globe, we find that the latter produce 9.5 parts carbonate of lime in solution at the same time as the remaining area of the land 3×95 or 285 parts. According to this calculation the river-waters which are discharged into the ocean contain on an average 74 mgrms. carbonate of lime per litre and carry every year 2 billions (or 2×10^{12}) K.G. carbonate of lime into the ocean, a value already mentioned in my first paper, though not yet explained.

According to this estimate the quantity of the calcium carbonate newly formed every year amounts only to a thirtieth (more exactly $^1/_{31}$) part of the total quantity which the ocean receives every year. Annually there are thus formed from silicates 64.5 milliards (or 64.5×10^9) K.G. of calcium carbonate, containing 28.4 milliards (or 28.4×10^9) K.G. of CO_2 in stable combination.

The earth having been evolved from a white hot liquid state, by cooling, and consequent envelopment with a solid crust, to its present state, we must assume that all the carbonate of lime arose

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from the silicates of that crust. Silicic acid, being present in very great surplus in the crust of the earth, would, as is well known, already at boiling temperature of water have decomposed eventually extant carbonates. The formation of the crust, however, must have begun about 1000° C., for the melting-points of most silicates are between 900° and 1500° C.[1]). The carbonates, therefore, can only have come into existence after the formation of a solid crust of already considerable thickness. As shewn by Lord KELVIN, rather soon after beginning solidification the temperature at the surface of the earth must have been almost exclusively under the influence of the radiation of the sun. At the end of 100 years this temperature may have been about 8° C. higher, and at the end of 100 centuries 0.8° C. higher than without underground heat [2]). We therefore may take it for granted that, considered from a geological point of view, the formation of the carbonates from silicates was initiated at the same time with the beginning of the condition of temperature, which made the earth an abode fitted for life.

If, therefore, we did know the average progress of this formation process as well as the total quantity of carbonates now extant, we should also know the time which has elapsed since the earth became fitted as an abode for life. As concerns the quantity of carbonates, besides the calcium carbonate, only the magnesium carbonate has to be taken into consideration; the other carbonates exist in relatively so small quantities, that in the very approximative calculations, concerned here, they may be neglected.

The proportion of the quantities of CO_2 in combination, as $CaCO_3$ and as $MgCO_3$, is for the water of the Rhine at Mayence [3]) probably about 3.3, for that of the Meuse at Liege 5.08, of the Danube at Vienna 2.36, of Thames [4]) at Kingston 8.33, of the Seine [5]) at Paris 5.17, of the Loire [6]) at Orleans 6.62, of the Spree [7]) above Berlin

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[1]) J. Joly, The Melting Points of Minerals. Proceedings R. Irish Academy 1891, II., p. 44.

[2]) On the Secular cooling of the Earth. Transactions of the Royal Society of Edinburgh, Vol. 23. Compare also Lord KELVIN's latest paper on the subject: On the Age of the Earth. Annual Address for 1897 of the Victoria Institute of London, p. 21.

[3]) According to the analyses during a year by E. EGGER (Chemisches Centralblatt 1888, p. 1131 and Ref. in Jahresber. über die Fortschritte der Chemie. 1888, p. 2762.)

[4]) WITT, l. c., p. 116.

[5]) POGGIALE, ref. in Jahresber. über die Fortschritte der Chemie für 1855, p. 833.

[6]) BISSCHOF, l. c., p. 273.

[7]) ROTH, l. c., p. 457.

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7.09 of the Vistula [1]) at Culm 5.28 of the Nile at Caïro probably about 3.00, of the Blue Nile at Khartoum 1.97, of the Syr-Darja 0.96, of the Rio Negro [2]) at Mercedes in Uruguay 5.44, of Lake Peipus 3.68, of the Lake of Geneva 3.08, of the Lake of Zurich [3]) 3.92, of the Lake of Bourget 4.42, of the Lake of Annecy 5.69 of St. Lawrence River 2.66, of the Lake of Gmunden 2.97, of the Lake of Saint-Point [4]) 11.55. The mean proportion in these twenty waters, which flow over true sedimentary formations, and are saturated with calcium carbonate, is 4.63. If this proportion, in which both carbonates are redissolved from sedimentary strata, also indicates the proportion in which they formerly originated in silicates, about $^1/_6$ of the CO_3 consumed in the evolution of the carbonates would have been taken by MgO.

It appears to me that the following considerations may lead to an approximative estimate of the quantity of the carbonic acid consumed and fastened in these carbonates.

It is most probable that all the oxygen, which now partakes of the composition of the atmosphere, and even more, has entirely orginated in carbonic acid gas through the assimilation process of the plants. In the rocks composing the earth's crust there is a great deficiency of chemically fixed oxygen, which would not be the case if in the former, hot, state of the earth there had been a sufficient quantity of oxygen available. According to CLARKE's analyses [5]) the rocks which compose the earth's crust consist on an average of 3.44 pCt. of FeO, thus an incompletely oxydized combination of iron. From the analyses of 83 basalts and diabases, published by ZIRKEL [6]) and ROSENBUSCH [7]), a mean percentage of 6 FeO is to be calculated, from the analyses of 29 granites a mean of 1.5 pCt., of 47 gneisses a mean of 3.8 pCt. Starting from the proportion given by CLARKE we may estimate, that all the O of the atmosphere would

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[1]) BISCHOF, l. c., p. 275.

[2]) SCHOELLER, l. c., p. 1787.

[3]) ROTH, l. c., p. 457.

[4]) The Lake of Saint-Point, through which the Doubs flows, and whose water, having a volume of 81,6 millions of M^3., is renewed in 205 days, contains, according to DELEBECQUE (Les Lacs français, p. 202) 136.4 mgrms. $CaCO_3$ per litre of water.

[5]) F. W. CLARKE, The relative Abundance of the Chemical Elements. Bulletin 78, United States Geol. Survey. Washington 1891, p. 37 and Ibid. No. 148. 1897, p. 12.

[6]) F. ZIRKEL, Lehrbuch der Petrographie. Zweite Auflage, Leipzig 1893. Band II, p. 29 and p. 901; Band III, p. 80 and 223.

[7]) H. ROSENBUSCH, Elemente der Gesteinslehre, Stuttgart 1898, p. 78, 308—309 and 468—471.

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only be sufficient to oxydize the FeO that is contained in the earth's crust to a depth of less than $^1/_2$ K.M. All the parts of the crust, which are no true sedimentary formations, up to the surface, are, however, rich in FeO.

In the reduction of carbonic acid through the plants there having been made free an equal volume of oxygen, and the oxygen in the atmosphere having a volume 700 times as large as that of the carbonic acid therein, there must have been in or passed through the atmosphere at least 700 times as much carbonic acid as it contains at present. Another quantity of the oxygen made free through the agency of the plants, which quantity it is impossible to estimate, was certainly consumed for the oxydation of FeO and other constituents of the crust which are poor in oxygen.

It appears, therefore, that when the earth was in the white hot fluid state there could not exist any free oxygen. That which was not combined with carbon or hydrogen would have been taken by FeO, and as there is still much FeO, certainly to a depth of many K.M., in the earth's crust, apparently at the beginning formation of that crust no free O can have been in the atmosphere. The quantity now in the atmosphere must be rather less than that formed from the consumption of free CO_2 reduced through the agency of the plants, for younger sediments are certainly poorer in FeO, and must therefore have consumed O. There has, however, at the same time with that oxydation, taken place reduction of combinations of iron by organic matter. The clay deposited by the Rhine in the Delta of the Lake of Constance contains, besides 1.66 pCt. organic matter, 3.23 pCt. FeO; slates from the carbonic formation, besides 0.7 pCt. organic matter, 4.73 pCt. FeO [1]). In consequence of this reduction again CO_2 is coming into the atmosphere, from which again O is set free through the agency of the plants. So from 1 volume of CO_2, which originally was in the atmosphere, there may be formed 2 or more volumes of O [2]). That reduction of Fe_2O_3 combinations takes place on a grand scale is proven by the existence of the blue mud, which covers an area 37.6 millions of K.M.^{2} or more than $^1/_{10}$ of the floor of the ocean, and which owes its colour to organic matter and FeS_2. Also the slates contain much FeO; as the mean percentage of 16 slates, of which the analyses are given by CLARKE, 3.25 is to be computed. In the waters of the larger rivers and

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[1]) ROSENBUSCH, l. c., p. 413.

[2]) Of course only a superior limit for the amount of coal and other carbonaceous remains of organic origin in the earth's crust may be deduced from the 700 a parts of CO_2, which have passed through the atmosphere, as the C of these has, in such a manner, been made use of several times.

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lakes, on the contrary, are to be found in solution combinations of Fe_2O_3 only.

But whatever may be the source of the CO_2, from which the O of the atmosphere has been set free through the assimilation process of the plants — for another process, which can produce O on a large scale in nature we cannot imagine — we must take it for granted, that an equal volume, that is at least 700 times the quantity of free CO_2 now extant in the atmosphere, has been in it, and most probably has gradually passed through it. Now too the supply of carbonic acid, through the volcanic activity of the earth (which certainly is the chief source) and the consumption, through the fossilisation of carbonaceous organic remains, and in still much higher degree that through the formation of carbonates, which according to the above made estimate now annually requires $\frac{1}{75400}$ of the quantity of carbonic acid in the atmosphere [1]), take place gradually. In all past times that consumption, as is shewn by the immense carbonaceous formations of organic origin and mighty strata of carbonate rocks, has been so large that we hardly can imagine but that this consumption and the supply from the interior of the earth have been equipoising processes.

Now SCHLŒSING [2]) has shewn, that for water which keeps in solution other salts (of natrium, magnesium, calcium) the quantity of the bicarbonate formed may be different from that formed in pure water, but that nevertheless, as in the latter case, it increases with the tension of the carbonic acid gas, so that there arises again a state of equilibrium between it and the tension of the carbonic acid gas. SCHLŒSING, further, pointed out that in the water of the ocean, which since many thousands of centuries has been in contact with the atmosphere and with the calcium carbonate of its floor, its shore and the supply of the rivers, there is a continual tendency to acquire this equilibrium. Variations in the quantity of the carbonic acid of the atmosphere will cause emission of carbonic acid from the ocean-water and severing of solid carbonate, if the variation is a decrease, or absorption of carbonic acid and dissolving of carbonate, if the variation is an increase. SCHLŒSING then calculated the quantities of carbonic acid contained in free state in the atmosphere, and in

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1) The amount of the carbonic acid in the atmosphere is taken in this calculation at 2140 billions KG. (which value is equal to 75400×28.4 milliard) from the averages stated below for the percentage of carbonic acid and the atmospheric pressure.

2) TH. SCHLŒSING, Sur la constance de la proportion d'acide carbonique dans l'air. Comptes rendus des séances de l'Académie des Sciences. 1880. Tome 90, p. 1410—1413.

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loose chemical combination in bicarbonate in the ocean. He found that the ocean keeps in reserve, and at disposal for exchange with the air, a quantity of carbonic acid ten times as large as the total quantity which the atmosphere contains, and concluded therefrom that the ocean exercises a regulating influence on the quantity of the carbonic acid of the air, acting as a reservoir which holds a quantity of carbonic acid at disposal very much larger than the quantity which constitutes the variation in the air.

The volume of the water of the ocean is, however, much larger than SCHLŒSING had assumed. Computed from the most recent and reliable data for the area and the mean depth of the ocean it comes to 1300 million K.M^3. If we accept the mean quantity of loose carbonic acid of 43.6 mgrms. per litre of ocean-water, according to DITTMAR, the mean atmospheric pressure at the surface of the earth of 740 mM. and the mean percentage of carbonic acid in the air, in volume, for both hemispheres, according to MÜNTZ and AUBIN [1]), of 0.027385, we find that in the ocean there is, in combination as bicarbonate, 26,5 times as much loose carbonic acid and also 26.5 times as much carbonic acid in stable combination as in the air in free state. Starting from the whole quantity of 55 mgrms. carbonic acid in stable chemical combination per litre of ocean-water, stated by DITTMAR, or from that of 53 mgrms., according to other statements, we further find, that in the water of the ocean 33.4 or 32.2, say 33 times, as much carbonic acid is in solution, in stable combination in calcium carbonate and bicarbonate, as the quantity of the free carbonic acid contained in the atmosphere. The quantity of the bicarbonate, however, alone is dependent on the pressure of the carbonic acid.

There being in the ocean 26.5 times as much loose carbonic acid as contained in free state in the atmosphere, the ocean has of every variation in the total quantity of carbonic acid by far the largest share. Of 27.5 parts carbonic acid which are to be disposed of or which are consumed, it always takes or gives 26.5 parts, and it has done so as long as its volume, its composition and its mean temperature and the pressure of carbonic acid did not differ much from the present state. Slight modifications of the pressure of carbonic acid, such as most probably have only taken place, can neither have had any noticeable influence. If, in fact, the quantity of the free carbonic acid in the atmosphere even changed with 60 pCt., the quantity of the carbonic acid taken up by the ocean in loose combination, according to the

[1] l. c., p. A 82.

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law of SCHLŒSING, would only vary with 16 pCt. or about $^1/_6$. Calling the quantity of the loose CO_2 in the ocean o, that of the free CO_2 in the atmosphere a, we find that $\frac{o}{a}$ would come to 19.23 instead of 26.5. To 1 part of free CO_2 in the atmosphere, the ocean would then only contain 19.23 parts of loose CO_2 in combination as bicarbonates, i. e. 0.725 of the actual proportion. In order, however, to cause this variation of 60 pCt. in the pressure of the carbonic acid in the atmosphere, the production or the consumption should undergo a variation of 0.6×19.23 or more than 11.5 times the quantity of carbonic acid at present in the atmosphere. Variations of the quantity of carbonic acid in the atmosphere of so great an amount, that they might have considerable influence on the value $\frac{o}{a}$ are therefore indeed highly improbable, as it appears that the consumption of carbonic acid regulates itself after the production.

As pointed out by HOGBÖM [1]) production of carbonic acid chiefly takes place by volcanic exhalations and geological phenomena connected therewith, and consumption by the formation of carbonates from silicates on weathering. "As the enormous quantities of carbonic acid, representing a pressure of many atmospheres, that are now fixed in the limestone of the earth's crust cannot be conceived to have existed in the air but as an insignificant fraction of the whole at any time since organic life appeared on the globe" the consumption through formation of carbonates and the storing up in sedimentary formations of carbonaceous remains of organisms must have been compensated by means of continuous supply, that is to say the two processes must always have nearly counterbalanced each other. May it be that the mentioned source of carbonic acid has not flowed regularly, but, just as single volcanous, has had its periods of relative rest and intense activity, and has produced now less, then again more carbonic acid, on the other hand also an increase of the supply surely causes an increase of the consumption. But even the relatively slight alterations of the quantity of carbonic acid in the air, which according to HOGBÖM may still be allowed, are entirely prevented by the vegetable world. The decomposition of CO_2 through the green plants varies with the tension of that gas in so high a degree, and the absolute quantity of CO_2 which annually is decomposed by the vegeta-

[1]) Quoted by S. ARRHENIUS, On the Influence of Carbonic acid in the Air upon the Temperature of the Ground. Philosoph. Magazine. Vol. 41, (1896) 5th. Series, p. 372.

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tion is so large (namely about $^1/_{20}$ of the whole quantity in the atmosphere) that soon the former percentage of CO_2 in the air, on which plant life is regulated, would be restored.

On account of the facts discussed in this and in my first paper we may assume, that certainly not more than one thirtieth part of the carbonate of lime, which the rivers now discharge into the ocean is newly formed from silicates. In the past, when still more silicate rocks lay uncovered at the surface of the earth, this quantity must have been larger. At the time the earth's crust consisted still entirely of them, the carrying of newly formed carbonate of lime would, under otherwise similar circumstances, certainly not have been more than *one eighth part* of the quantity of the carbonate of lime now carried by the rivers to the ocean, and which is by far the greater part only circulating (redissolved) carbonate of lime. As the silicate rocks have gradually been covered with sedimentary strata that proportion must gradually have got smaller. If we take the most simple and most probable case, that this decrease took place proportionable to the time, then on an average 0.08 of the present annual carrying of calcium carbonate by the rivers would every year have been newly formed, thus 160 milliards (or 160×10^9) K.G., containing 70.4 milliard (or 70.4×10^9) K.G. of CO_2 in stable combination.

In the long run the consumption of CO_2 for the formation of carbonates from silicates and that for the formation of oxygen are to be considered as two processes, parallel in their magnitude, which, if other circumstances do not vary, are dependent on the pressure of the carbonic acid in the atmosphere. It is clear that the oxygen which only circulates through the plants is not concerned here. the circulating oxygen again serving for the oxydation of organic matter, just as the circulating calcium carbonate does not consume any carbonic acid, there being used for the formation of bicarbonate as much as is set free again when it returns into the solid state. However, to 700 *a* parts of free carbonic acid, consumed for the storing up of oxygen, in the atmosphere, 26.5×700 or 18550 *a* parts must have been liberated from bicarbonates in the ocean, and thus at least 18550 *a* parts of carbonic acid in loose, and an equal quantity in stable chemical combination have been in bicarbonates redissolved from solid carbonates.

When thus at least 700 *a* parts of free carbonic acid in the atmosphere have been turned into oxygen, there must have been consumed in the waters of the rivers and the ocean at least $26.5 \times 700 \times 0.08$ or 1484 *a* parts carbonic acid for the carbonates newly formed from silicates. Thus we find that, from the time the globe, by cooling, has been sur-

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rounded by a solid crust, *at least* 7.22 trillion (or 7.22×10^{18}) K.G. calcium carbonate have been formed which, equally spread over the whole area of the land of the globe, would be able to form a layer of limestone everywhere about 20 M. thick [1]). Of course this is only a minimum, as the value 700 *a* also is a minimum. According to the estimates of MELLARD READE [2]) and DANA [3]) the mean thickness of the limestone under the land area of the globe would be 28 to 52 times as large. Assuming that the rivers carry to the sea on an average 450 mgrms. per litre or 6 times as much matter in suspension and in solution as they do carbonate of lime in solution, this proportion would lead us to impute to the sedimentary rocks under the continental areas an average thickness of about 3000 to 6000 M., certainly no too high estimates.

The time required for the evolution of that minimum amount of carbonate of lime from silicates it is, after these considerations, very easy to estimate.

In the same way as the quantity of the bicarbonates in the ocean, the average quantity of the bicarbonates in the river-waters is dependent on the pressure of the carbonic acid in the atmosphere. So the *ratio* between the average quantities of the bicarbonates, which the rivers have annually carried into the ocean, and the total of those which were in solution in the ocean is independent of the pressure of the carbonic acid in the atmosphere. Whatever variations the pressure of that gas in the atmosphere may have undergone, at any time in the past history of the earth the ratio between the quantities of those salts in solution in the ocean-water and the river-waters was not changed thereby. Further there must exist between the total quantities of the redissolved and the newly formed bicarbonates, which in the ocean have ever passed from the dissolved into the solid state, the same ratio as in the river-waters, for the ocean-water owes its provision of those salts to the rivers. As now the rivers carry annually two billion K.G. calcium carbonate in solution, containing $\frac{1}{2432}$ *a* carbonic acid, a total amount of 18550×2432 or 45 million times that quantity, in combination in calcium carbonate, has in the ocean passed from the dissolved into the solid state.

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[1]) Reckoned on a basis of 8 pCt. impurity.

[2]) Limestone as an index of Geological Time. Proc. Royal Soc. Vol. 28. London, 1879, p. 281.

[3]) L. c.

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Therefore the formation of the whole estimated minimum amount of carbonate of lime on the earth would require about *forty-five millions of years*, that of the real amount, however, a very much larger lapse of time.

It appears, furthermore, that $\frac{1}{2.770.000}$ of the total quantity of the carbonate of lime of the earth participates annually in the present circulation.

The amount of carbonic acid corresponding to the limestone rocks and carbonaceous formations in the earth's crust has been estimated very differently, namely between 12.000 and 15.0000 times the quantity of free carbonic acid contained in the atmosphere. The newest estimates differ somewhat less from one another. HÖGBOM [1]) considers it as probably underestimated, if we take that 25000 as much carbonic acid is fixed in the limestone of the sedimentary formations as exists in free state in the atmosphere. DANA [2]) calculates the quantity of carbonic acid, corresponding to the limestone and to the coal, mineral oils and gasses in the earth's crust on 45 atmospheres, that is 100.000 times the quantity of free carbonic acid in the atmosphere. CHAMBERLIN [3]) estimates, without indicating his method, that quantity on 20.000 to 30.000 *a*. At all events these geological estimates all differ too much from the minimum of 1484 *a*, calculated above by indirect way, that the presumption should not been raised — if indeed the bases of these estimates are in some degree reliable — that the value 700 *a*, from which the present calculation started, is only a minimum, and that indeed very much oxygen from the atmosphere has been taken away by oxydation of substances in the earth's crust which are poor in oxygen.

On the calculated number of 45 millions of years some corrections are to be made. Firstly this number should be diminished with at least a sixth part, because the carrying of carbonate of magnesia through the rivers has not been taken into account. Secondly the eroding agency of the ocean has not been considered; the ocean too assailing, at its border, silicate rocks and the forming of carbonates taking place there too. But thereby the number can decrease only little, as the eroding influence of the ocean is but slight compared to the agency of the waters on the land. DE LAPPARENT [4]) estimates

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[1]) l. c. p. 271.

[2]) J. D. DANA, Manual of Geology. Fourth Edition. New-York 1896, p. 485.

[3]) T. J. CHAMBERLIN, Journal of Geology, Chicago 1897, p. 656.

[4]) A. DE LAPPARENT, Traité de Géologie. 4me Édition. Paris 1900, Tome I, p. 242.

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the proportion on less than 1 : 10 and JOLY [1]) even on 1 : 177. Thirdly the rivers may have discharged more water during the prevailing of warmer climates, thus during the longest time of the past of the earth. Neither can this influence, by which the stated number would get smaller, have been considerable, for, according to figures given by MURRAY [2]) the rivers under the present conditions discharge — at equal drainage area — in the area of the land between 30° North and 30° South of the equator on an average only 1.55 times as much water as outside of the 30° North and South. It therefore would certainly be too high an estimate assuming that, at the time when over the whole earth a tropical climate prevailed, the discharge of water, and therefore too the carrying of calcium carbonate (which at higher temperature of the water is even somewhat less soluble) had been one and a half time as high as at present. Fourthly the weathering of silicates and the formation of carbonates may have been more rapid on account of the temperature having been on the whole higher, of a more abundant supply of carbonic acid or of more rapid changes in orographic and hydrographic conditions. These factors too would diminish the stated number, but probably not considerably. Fifthly the ocean has originally been less salt; though already in such old formations as the cambrian mighty beds of rock-salt occur, a proof that in this factor is not to be sought the cause of important changes in the absorbing power of the ocean for carbonic acid, and therefore, by modifying the proportion $o : a$, of the time required for the formation of the limestone rocks, a modification that would also diminish the stated number. Sixthly a higher average temperature of the ocean-water would decrease the proportion $o : a$; at a homogeneous tropical climate of the earth probably about 20 pCt., with which amount the estimated time also would have to be diminished. Seventhly the volume of the ocean-water could have decreased; but the analyses of the rocks show that in such a manner at most a decrease of a few hundredths parts could have taken place. On the contrary much water is produced in volcanic exhalations and connected geological phenomena.

All those influences, however, which would decrease the result of this time estimate, apparently do not counterbalance together the one influence of the loss of oxygen from the atmosphere by the oxydizing of Fe O and similar substances poor in oxygen, so that

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[1]) An Estimate of the Geological Age of the Earth. Scientific Transactions Roy. Dublin Society. Vol. VII (Series II). Dublin 1899, p. 63.

[2]) l. c., p. 70.

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it appears, that we may assume, that the formation of the carbonates from silicate rocks has required *at least some decuples of millions of years*, and this the earth's crust also exists at least the same length of time. But this is a minimum; the real lapse of time since the formation of a solid crust and the appearance of life upon the globe may be *more than a thousand million of years*.

This final result of the investigation, however little claim it may make to exactness, might nevertheless interest geologists and biologists, who generally demand such a vast space of time. Moreover this result would be of some importance, if it should suggest nearer trial of the so called physical methods of estimating the age of the earth, by which Lord KELVIN has acquired unperishable merit for geology and biology, a trial which in many other respects too is desirable and promises important results. In his already quoted latest paper on this subject [1]) Lord KELVIN estimates the age of the earth's crust, on the basis of these methods, at about 24 millions of years, and the sun he estimates about as old. It seems possible to modify some factors in the calculations of Lord KELVIN in such a way that higher results are obtained. The here sketched geological method appears to confirm that opinion. May it therefore be further worked out and lead to a more exact estimate of the age of the earth as an abode fitted for living beings than the estimates hitherto obtained.

Zoology. — "*Further results of an investigation of the Monotreme-skull*". By J. F. VAN BEMMELEN, The Hague (Communicated by Prof. C. K. HOFFMANN).

I. *Palate.*

In a former note [2]) the curious fact was mentioned, that in the Echidna-skull the pterygoids form part of the floor of the cerebral cavity, filling up a gap between the body of the sphenoid bone and its posterior or temporal wings (alisphenoids), so as to be visible on the inner side of the skull-bottom. To this we may now add, that the same is the case with the palatine bones. In a skull, in which the majority of the sutures could still be distinctly traced, a slender porterior process of the palatine was seen running down on

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[1]) On the Age of the Earth, p. 11 and 25.

[2]) These Proceedings. October 25th 1899. p. 81.

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either side of the sphenoid body, separating it from the pterygoid. Both palatine and pterygoid took part in the formation of the median border of the oval foramen, the palatine forming the anterior, the pterygoid the posterior part of this border. Only at a very advanced stage of growth, the lateral border of the foramen in question also gets closed up by bone, i. e. by that thin bony plate, which in my opinion must be considered as representing the alisphenoid (l.c. p. 82). The antero-median angle of this ossification reaches the posterior border of the curious temporal wing of the palatine, likewise mentioned in my first note.

Of course only that part of the palatine is visible at the inner side of the skull-bottom, which is not overlapped by the body of the sphenoid. This part amounts to about the lateral third of the posterior palatine processus (situated behind the temporal wing). The middle strip is covered by the side-border of the corpus sphenoidei, while the inner or medial third-part projects as far as the middle line of the skull forming the floor of the nasal canals. It is well-known, that in Echidna this floor is incomplete, the palatine plates diverging posteriorly, so as to leave open between them a deep fissure which however, in Proëchidna, is reduced to a mere concavity of the transverse hind-border.

It needs hardly to be specially mentioned, that the participation of membrane-bones of the roof of the buccal cavity, such as the palatines and pterygoids, to the formation of the floor of the cerebral skull, can only be explained by the supposition that the primary cartilaginous skull-floor has suffered complete reduction within the limits of these bones. At the same time this hypothesis gives an explanation of the fact, that the ali-sphenoids do not reach the corpus sphenoidei: the cartilage, that was to bring about this connection having disappeared early instead of ossifying. The same phenomenon must have occurred on the outer side of the region of pterygoids and palatines, leading to the formation of the great gap or fontanella in the temporal area of the skull-wall, which is so characteristic for young Echidna-skulls. The alisphenoidal ossification, which finally closes up this gap, must thus develop in membrane, and must permanently remain separated from the corpus sphenoidei.

The probability of this supposition receives a firm support by the comparison with the skull of the Echidna-pouch-suckling. This shows the primordial cartilage still in situ under the osseous pterygoids and palatines, though it is totally absent in the region of the above-mentioned temporal fontanella. The final disappearance of this cartilage, leading to the entrance of pterygoids and palatine-processes

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into the composition of the skull-floor, must therefore occur at a relatively advanced stage, at all events after birth.

II. *Squamosal.*

In a recent publication [1]), Prof. V. SIXTA, has made a comparison between the skulls of the Monotremes and that of Psammosaurus griseus, and has come to the conclusion, that the former agree with the latter in most respects, notably in the possession of a quadrate bone. In Ornithorhynchus this bone is said to bear the glenoid surface for the under-jaw, in Echidna, on the contrary, it is said to form a bony bridge on the ventral side of the stylo-mastoid foramen.

In order to verify the correctness of this assertion, I once more looked over my material of young and adult Monotreme skulls, but I was not able to find any trace whatever of a separate quadrate bone, not even in the skulls of newly-born (or still unborn) sucklings. Moreover the osseous bridging over of the stylo-mastoid-foramen mentioned above is no peculiarity of Echidna alone, but occurs as well and in the very same spot in Ornithorhynchus, with only this restriction, that it does not completely surround the ventral side of the foramen, but leaves open a small gap at the medial side.

If therefore this bone-bridge did really represent the Reptilian quadrate, the same designation could never be applied to a far more laterally-situated part of the Ornithorhynchus-skull. In my opinion however we have no right at all to consider either part of the Monotreme skull as a quadrate: the glenoid fossa of Ornithorhynchus simply forming the ventral face of the squamosal, whereas the bony bridge under the facialis-foramen of both genera is a part of the mastoid, and must be called the processus mastoideus. SIXTA, in Ornithorhynchus, calls it the processus paramastoideus, which name, according to my views, is wrongly applied as it must be retained for an outgrowth of the exoccipital (pleuro-occipitale or occip. laterale) occurring in many mammals, and not be given to a part of the mastoid.

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1) SIXTA, V. Vergleichend-osteologische Untersuchung über den Bau des Schädels von Monotremen und Reptiliën. Zoologischer Anzeiger. Bd XXIII N°. 613. 23 April 1900.

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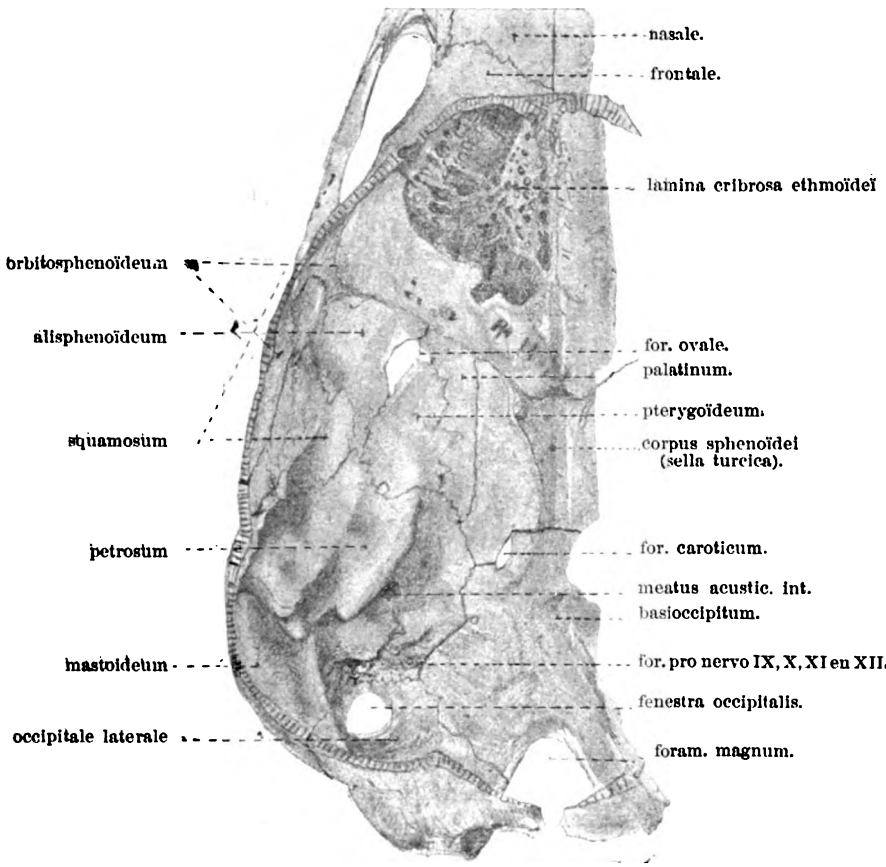
J. F. VAN BEMMELEN. Further results of an investigation of the Monotreme-skull.



Echidna hystrix. Floor of the cerebral cavity, left side, inner aspect $^{2}/_{1}$.

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Chemistry. — "*On Soap Solutions.*" By Dr. A. SMITS (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

Determinations of the boiling point of concentatred solutions of soap, made by E. KRAFFT [1]) in BECKMAN's apparatus, have lead to the surprising result that the boiling point of a concentrated solution of soap is identical with that of pure water.

On account of this phenomenon, KRAFFT has proposed to classify soaps among the colloids, which induced L. KAHLENBERG and O. SCHREINER [2]) to investigate aqueous solutions of soap in a physico-chemical direction.

They first of all applied the method of boiling, but they found in agreement with the experiments of KRAFFT, that, when using BECKMAN's apparatus, a concentrated solution of soap boils at the same temperature as pure water. If they did not apply a direct flame but heated by means of a paraffin bath at 125°, the boiling point was 0.191° lower than that of pure water.

From these observations they came to the result, that they were not dealing here with a simple boiling phenomenon and called the boiling of a soap solution „Pseudo-Boiling".

Abandoning the method of boiling, they have determined the electrical conductive power of *dilute* solutions of soap at 25° and have found that these solutions are all good conductors of the electric current, from which they have rightly concluded, that *these* soap solutions cannot be classed among the colloids. In my opinion they have, however, overlooked the significance of the dilution. The greatest concentration mentioned in the tables amounts to $^1/_4$ gram mol. per litre in the case of sodium oleate, whilst it amounts to $^1/_{64}$ gram mol. for potassium stearate and $^1/_{16}$ gram mol. per litre for potassium palmitate.

Greater concentrations could not be investigated at 25° on account of gelatinizing setting in. They state to have convinced themselves that solutions of soap containing more than $^1/_4$ gram mol. per litre are good conductors of the electric current at temperatures at which they are liquid but they do not say how great those concentrations have been.

KAHLENBERG en SCHREINER have also determined the lowering

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[1]) Ber. d. d. chem. Ges. 27, 1747 (1894).
Ber. d. d. chem. Ges. 28, 2566 (1895).
Ber. d. d. chem. Ges. 29, 1328 (1896),

[2]) Zeitschr. f. Phys. chem. 27, 552 (1898).

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of the freezing point of dilute solutions of sodium oleate. The greatest concentration was $^1/_8$ gram mol. per litre. The results obtained indicate that the investigated solutions contained double-molecules.

In a subsequent treatise entitled: „Ueber das Sieden wässeriger colloidaler Salzlösungen"[1]) in which KRAFFT says nothing about the researches of KAHLENBERG and SCHREINER except that they are „höchst unzweckmässig ausgeführte Versuche", he communicates a series of boiling point determinations of different more or less concentrated solutions. The general result is that concentrated solutions of soap have the same boiling point as pure water. In order to prove that the boiling of the soap solutions proceeded normally, a small quantity of sodium chloride was added to the boiling solution after which a normal elevation of the boiling point was generally noticed.

As KRAFFT, to prevent burning, was obliged to introduce into his boiling vessel large glass beads at a height of only 12—15mM. instead of a 5 cM. layer of "shot", the boiling water must have been considerably superheated. To avoid this error I have made some boiling point determinations of solution of sodium palmitate with my recently described boiling apparatus[2]). Superheating or burning is completely avoided when using this apparatus.

The sodium palmitate used by me was prepared from very pure palmitic acid according to KRAFFT's method. The soap contained 8.26 per cent of Na, theory requiring 8.27 per cent.

It was to be expected that, with the new method of boiling, the soap solution would froth dreadfully. By various devices I have tried to limit this frothing so as to prevent the lather from leaving the boiling vessel but I have not been able to find satisfactory means and so I finally did not trouble about the lather.

After the maximum temperature had been read off, a few were pipetted out of the boiling vessel and weighed. The concentration of this weighed solution was determined by warming with an excess of standard sulphuric acid, until the palmitic acid had completely melted and separated on the surface of the liquid. When cold, the solution was filtered and the excess of sulphuric acid titrated with standard potassium hydroxide.

I experienced all the same that the frothing of the soap solutions, when experimenting in this manner, was a great nuisance particularly

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[1]) Ber. d. d. chem. Ges. 32, 1584 (1899).

[2]) Proc. Royal Acad. Amsterdam, May 26, 1900 p. 31.

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when dealing with concentrated solutions, because the frothing is then so excessive that, unless the steam is passed exceedingly slowly through the solution, hardly any will be left in the boiling flask. I have, therefore, been obliged to pass an extremely slow current of steam particularly when dealing with more concentrated solutions. The result is consequently less accurate than I desired.

In this way. I found:

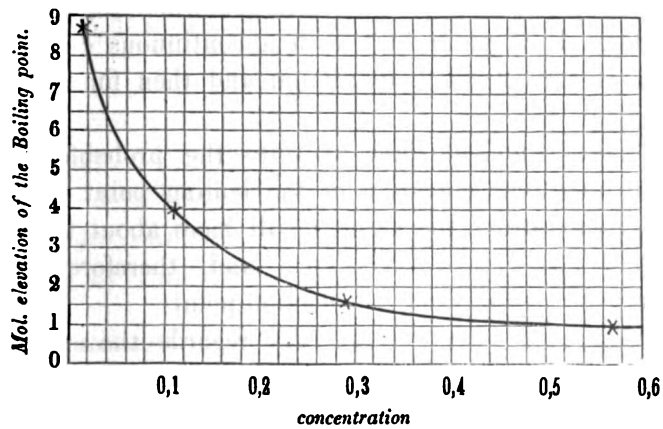
SODIUM PALMITATE.

Concentration in gr. mols. per 1000 gr. of H_2O.	Elevation of the Boiling point.	Mol. elevation of the Boiling point.	
0.0282	0.024	8.6	Normal. 5.2
0.1128	0.045	4 0	
0.2941	0.050	1.7	
0.5721	0.060	1.0	

From this it is seen that the molecular elevation of the boiling point continually lowers with the increase of the concentration.

The annexed graphic representation shows that the curve of the mol. elevation of the boiling point approaches the concentration axis.

Fig. 1.



To trace the point where this curve practically meets the concentration axis. I ought to have determined the boiling point of still more concentrated solution, but when doing this in the manner described the intense frothing is such a nuisance that I was obliged to abandon the plan.

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In order to study the behaviour of more concentrated soap solutions, I have applied the method of vapour tension. For that purpose one of the bulbs of a Bremer oil-tensimeter was filled with sodium palmitate and water and the other with pure water. After the instrument had been evacuated by means of an automatic mercury air-pump it was sealed, furnished with a glass scale and placed in a waterbath the temperature of which was kept constant at 80°. In this manner the decrease in vapour tension of three different concentrations was determined.

The results were as follows:

SODIUM PALMITATE.

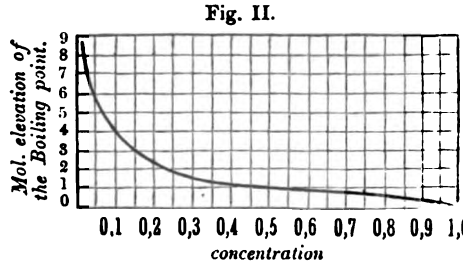
Concentration in gr. mol. per 1000 gr. of H_2O.	Decrease of Vapour tension in m.m. Hg at 0°
1.00	0.00
0.75	0.50
0.50	1.30

Whilst therefore the soap solution of 1 gram mol. concentration appeared to have the same vapour tension as pure water, the decrease of the vapour tension became larger when the concentration became smaller. It is plain that with a continuous decrease of the concentration it will reach a maximum and then finally fall again to zero.

We now have sufficient data to state the probable progressive change of the molecular elevation of the boiling point.

The curve representing the change will have about the following form and, therefore, have a inflection-point.

Fig. II.



As regards the explanation of this progressive change, I think this must be found in the strong diminution of the hydrolytic dissociation of the soap when the concentration increases.

The hydrolytic dissociation at the concentration of 1 gram mol. is practically *nil* which is also proved by the exceedingly small

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alkalinity of this concentrated soap solution. At this concentration we, therefore, have only a solution of the normal salt which does not seem to cause an elevation of the boiling point or a decrease of the vapour tension.

Summary of the Results.

It has been demonstrated by a combination of the methods of boiling point and vapour tension that solutions of sodium palmitate below the concentration of 1 gram mol. per 1000 grams of H_2O cause an elevation of the boiling point and a decrease in the vapour tension, which starting from the concentration 0 must reach a maximum to again become 0 at about a concentration of 1 gr. mol.

This progressive change which hitherto had not been carefully studied may be explained by the appearing and again disappearing of the hydrolytic dissociation.

As a concentrated solution of sodium palmitate has the boiling point and vapour tension of pure water, it may be rightly concluded with KRAFFT that this concentrated solution is colloidal.

KAHLENBERG and SCHREINER found that both dilute and concentrated solutions are good conductors of the electric current. From the foregoing it is plain that dilute solutions should be so. Concentrated soap solutions will probably be bad conductors of electricity. It will, however, be very difficult to prove this fact as for this purpose an absolutely pure material is required.

Amsterdam, Chem. Lab. University, June 1900.

Geology. — "*Leperditia baltica His. sp., their Identity with Leperditia Eichwaldi Fr. v. Schm. and their being found in Groningen diluvial erratics.* By Mr. J. H. BONNEMA (Communicated by Prof. J. W. MOLL).

In his Miscellanea Silurica I (Mém. Acad. St. Pétersbourg, VII Série, Tome XXI, N°. 2) and Miscellanea silurica III (Mém. Acad. St. Pétersbourg, VII Série, Tome XXXI, N°. 5) Mr. VON SCHMIDT describes i. a. Leperditia baltica His. sp., which then had not yet been found in the Russian Baltic provinces, but are frequently met with in Gotland in stones, whose age corresponds with that of the Lower Oesel Zone. He also enumerates the characteristics of a new species, viz. Leperditia Eichwaldi, which are declared to occur in

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dolomites of the Northern coast of Oesel, belonging to the Lower Oesel Zone.

Now, when in the collection of sedimentary erratics from „Hondsrug", that are found in the Geological Museum at Groningen, I gathered, in accordance with this description, the remains of Leperditia Eichwaldi Fr. v. Schmidt, it struck me, that they were represented by right valves only.

Attentive reading proved to me, that other persons had arrived at the same conclusion and seen the same phenomenon. I found that in the „Zeitschrift der Deutschen geologischen Gesellschaft" year 1891, pag. 489, Mr. Krause makes mention of a few right valves belonging to his collection, which valves he classes with Leperditia Eichwaldi. Mr. Kiesow too, in the „Jahrbuch der Königl. Preuss. geologischen Landesanstalt für 1889" describes on page 91 only a right valve of this species.

At the same time I observed, that of the species Leperditia baltica His. sp. many left valves (which may directly be known by the transverse striae on the outer part of their inverted ventral plate) are found in the above-named collection, but that right valves were very rare.

It seemed most improbable to me, that all this should have to be ascribed only to Chance; the more so as in a few erratics, in which both left and right valves are found, the former were said to be Leperditia baltica and the latter Leperditia Eichwaldi.

I supposed, therefore, that Leperditia Eichwaldi Fr. v. Schmidt and Leperditia baltica His. sp. had better be united. The circumstance, that they are of the same age, was entirely in accordance with this.

The very first thing I did was to try to explain, why transverse striae should be wanting on the ventral plate of the left valves of Lep. Eichw., by which the latter, according to Mr. von Schmidt, are distinguished from the left valves of Lep. baltica. An explanation was soon found in the circumstance, that the chief material of Mr. von Schmidt consisted of stone-kernels (casts) of Kiddemetz: for when I made a longitudinal section on the transverse striae of the ventral plate of a left valve of Lep. baltica, I found that the elevations on the lower side are not answered by corresponding grooves on the upper side. Consequently, no trace of strokes will be present on the cast.

After this, I traced the difference between the right valves of these two Leperditia-species. According to Mr. von Schmidt this difference consists in the right valves of Leperd. Eichw. being penta-

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gonal, as it has an obtuse projection in the midst of its belly-side. I found, that Mr. VON SCHMIDT had afterwards changed his opinion with regard to this. In „Einige Bemerkungen über das Baltische Obersilur in Veranlassung der Arbeit des Prof. W. DAMES über die Schichtenfolge der Silurbildungen Gotlands (Mélanges géologiques et paléontologiques tirés du Bulletin de l'Académie impériale des sciences de St. Pétersbourg, Tome I Livraison 1) he writes on pag. 124 the words, whose translation into English runs as follows: „The right valve of the pectinata (Lep. baltica) shows a more or less distinct projection in the centre of the belly-side." In accordance with this was the fact, that at Kiro (southward of the country-seat Tagamois) in Oesel, which place is also mentioned by VON SCHMIDT on page 123 of the same essay Lep. baltica had been found there — I had come across a right valve with a clearly visible projection.

Consequently I arrived at the conclusion, that Lep. Eichwaldi FR. v. SCHM. had to be united with Lep. baltica His. sp.

Not without satisfaction I now percieve, that Mr. VON SCHMIDT already shares my opinion, in part at least. In the above-named essay he tells the reader on page 133, that some of the specimens of KIDDEMETZ, at first described by him as being Lep. Eichw. belong to the Lep. baltica.

As far as the form of the carapace is concerned, Lep. baltica (Lep. Eichwaldi included) often resembles Lep. arctica Jones, sketched and pictured in Ann. and Mag. Nat. Hist. Serie III, Vol. 7, page 87, Pl. VII figs. 1—5. The eye-tubercle of this latter species is however, surrounded by a rhombic blot. The valves of Lep. baltica are thick and the sides are usually but slightly arched. They frequently run up regularly towards the centre, and consequently they become flat-conic. They show rather distinct points, which are put into a net-work of grooves, running out of the middle blot. The anterior and posterior margin run up rather steep. A flat marginal rim on the anterior and posterior borders is usually not to be seen; it is clearly perceptible only in large right valves, and the most clearly on the anterior margin.

As was already said before, the right valves possess in the middle of their ventral border a more or less strong projection, in consequence of which they become rather pentagonal in form. In those places, where the right valves of Leperditia grandis Schrenck has a round aperture, we find here several slit-like ones, the number of which is not easily fixed. In one case I count ten in front, in another I find six on the back-side.

The left valve may immediately be known by the transverse slit-

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like elevations, that are found on the outer part of the lower side of the inverted ventral plate.

The Groningen erratics, containing remains of Leperditia baltica, are limestones, varying between yellowish-grey and yellowish-brown. In these stones, or in others of exactly the same nature, are also found remains of Encrinurus punctatus Wahlenb. sp., Proetus concinnus Dalm. sp., var Osiliensis Fr. v. Schm., Calymene tuberculata Brünn., Cyphaspis elegantula Lov. sp., Bumastes barriensis Murch., Beyrichia spinigera Boll, Primitia seminulum Jones, Primitia mundula Jones, Strophomena rhomboidalis Wilk. sp., Strophomena imbrex Vern. (non Pander), Atrypa reticularis L. sp., Zaphrentis conulus Lindstr., Halysites sp. and Tentaculites sp. This proves sufficiently, that these erratics are of the same age with the Lower Oesel Zone. The comparing-material at my disposal does not enable me to come to a positive conclusion with regard to their origin.

Botanics. — "*Contributions to the knowledge of some undescribed or imperfectly known Fungi*" (1st Part). By Prof. C. A. J. A. OUDEMANS.

On entering upon the task which I have undertaken, I wish to express my kind thanks to Messrs. C. J. J. VAN HALL, Candidate in Botanics and Zoology at the Amsterdam University and Assistant to Professor Dr. J. RITZEMA BOS; Mr. C. J. KONING, Chemist at Bussum, one of my former disciples and author of an essay published by VAN HETEREN (Amsterdam) and ENGELMANN (Leipzig), and entitled: "Der Tabak. Studien über seine Kultur und Biologie", dedicated to Prof. Dr. J. FORSTER, Straatsburg, and to Mr. C. A. G. BEINS, private person at Nunspeet, who in different ways have helped me to facilitate that task, as well by the collecting and sending of objects, and the yielding of their observations there about, as, and this regards Messrs. VAN HALL and KONING by their putting at my disposal their drawing-pen and pencil, where I wanted these to elucidate here and there the text of my contribution. I highly value that help and am fully confident that in future it will not be denied me.

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I. ASCOMYCETAE.

PYRENOMYCETAE.

Sphaeriaceae.

a. Phaeodidymae.

DIDYMOSPHAERIA Fuckel.

1. DIDYMOSPHAERIA RHODODENDRI Oud. n. sp. — On branches of a cultivated exotic *Rhododendron*; Wassenaar, 1894.

Perithecia fere destructa. Asci perfecte cylindracei, subsessiles, 116 × 7 μ, paraphysibus quam plurimis filiformibus obvallati. Sporidia oblique monosticha, umbrina (Sacc. Chromotaxia, n°. 9), bilocularia, cylindrica, ad polos rotundata, vix constricta, 14 × 4 — 5 μ.

b. Phaeophragmiae.

LEPTOSPHAERIA Cesati et de Notaris.

2. LEPTOSPHAERIA GENISTAE Oud n. sp. On the pods of *Genista anglica*. — Nunspeet, 2 Jan. 1899; Mr. BEINS.

Perithecia innato-erumpentia, in maculis pallescentibus vulgo aggregata, nigra, $^1/_5$ mill. in diam., vertice p.m. depresso perforato; asci cylindracei, breve pedicellati, 8-spori; sporae distichae, amoene fuscae, 2-septatae (3-loculares), ad polos rotundatae, absque appendiculis, 14—18$^2/_3$ × 4$^2/_3$ μ, loculo intermedio leniter incrassato.

Sporulis 2-septatis a pluribus affinibus descissit.

3. LEPTOSPHAERIA PHLOGIS Oud. n. sp. — On the leaves of *Phlox decussata*, cultivated at Dedemsvaart, 10 Nov. 1898. — Sent by Prof. Dr. RITZEMA BOS.

Perithecia parva, sparsa. Asci cylindraceo-clavati, curvuli, sessiles, 46 × 9$^1/_3$ μ. Sporidia disticha, cylindracea, curvula, ad polos obtusa, 3-septata, loculo penultimo antico ceteris ampliore, fuscidula, 23—25 × 4—5 μ. (Pl. IV fig. 1).

4. LEPTOSPHAERIA VAGABUNDA Sacc. Fgi Ven. Ser. II, 318; Sacc. Mycol. Ven. p. 97 et tab. IX f. 37—46, sub titulo erroneo „Sphaeria fuscella"; Sacc. Syll. II, 31; Fabre Ann. Sc. nat. 6, IX, 89; Berlese Icones Fung. I, Fasc. II, tab. XLV f. 1; Penzig, Funghi Agrumicoli p. 30 et tab 1144 B; Winter Kr. Fl. II, 465; Oud. Ned. Kr. Arch. 2, V, 482 et 2, VI, 33; Oud. Rév. II, 288. (Pl. I fig. 1).

Ramicola. Perithecia corticola, sparsa vel aggregata, nigra, $^1/_5$—$^1/_2$ mill. in diam., depresso-sphaeroidea, ostiolo parum vel nequa-

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quam prominulo, primitus peridermate tecta, postremo exposita. Asci cylindraceo-clavati (*d*), breve stipitati, vertice rotundati, paraphysibus filiformibus copiosis obvallati, 8-spori, 132—154×22 μ. Sporidia disticha, primitus continua, hyalina, fusiformia, 4-guttulata; denique aeque hyalina, 2-locularia, ex partibus dimidiis conoideis conformata, singulis biguttulatis, basi sua sibi invicem arcte applicatis et coarctatis, infra apicem obtusum paullo collapsis; postremo cylindraceo-fusiformia, fuscescentia, quadrilocularia, ad septa constricta, recta vel curvula, nunc eguttulata, tunc vero loculo uno alterove guttula praedito, ad polos obtusata; sporidia hyalina $13^1/_2$, colorata $22^1/_2$ μ longa, ultima praeterea $4^1/_2$ μ lata; utriusque generis in iisdem ascis mixta, quum varia evolutionis stadia representent. Sporidia immatura mire simulant ea plurium specierum Diaporthes.

On branches of *Tilia*. Bussum and elsewhere in "het Gooi". March, 1900. Mr. C. J. KONING.

Though this fungus has long been known already, we have yet reserved a place to *L. vagabunda* in this essay, 1st because we have to give some particularities from the life of the fungus itself; 2nd as we wished to sketch the changes which its presence brings about in the more profound tissues of *Tilia*, and 3rd because we wanted to draw attention to the result of some experiments performed by Mr. KONING about the nature and virulence of the poison secreted by the mycelium of the fungus.

The infection of branches of limetrees by the spores of *Leptosphaeria vagabunda* manifests itself by small black spots on the surface of the green, or brown-red, glossy young branches, of which the youngest internodes are first attacked. They are shorter- or longer-oval, a half to one and a half centim. long, and some millim. wide, and in the middle they always show one or two white dots. By-and-by the black colour changes into a dark brown and the spots take the appearance of solid, brittle scales, which after shorter or longer time isolate themselves from the surrounding parts to resemble little isles which are separated from the rest by a circle-shaped groove, and finally also let loose the tissue underneath and fall off. Microscopic examination points out that they consist of flat table-shaped, brown air-bearing cells, and that their colour is due as well to a change of the cell-walls, as to a modification of their contents which is condensated to a shrivelled mass. The white dots are lacunae, filled with colourless, loosely contiguous globose cells, i.e. lenticels which, as in many other trees and shrubs, take the place originally occupied by a stoma.

The result of this research, combined with the appearance of the

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black spots, can lead to no other view but that the stomata or lenticels are the localities where the spores of a former generation came down and germinated, and that the germinal tubes secrete a poisonous substance which caused the above described changes.

It was obvious that these germinal tubes and the thence proceeding mycelium-filaments ought to be found out. On the very first prepared transverse sections of the black spots and the tissue underneath, it seemed, however, that this end could not be gained. Very rarely a mycelium filament came into sight, so that the impression arose that a destruction, as figured on our plate, was not in the least proportioned to the number of germinal tubes or mycelium-branches wanted to bring about so much mischief. Meanwhile, however, after the knife had been introduced in other directions, and in particular in a tangential one through the spots, and more inwardly, more and more filaments were discovered, so that the proportion between the damage occasioned, and the cause of it, appeared in a quite different light from what had been supposed at the beginning of the research.

Before coming to this result, rather much time had however got lost, apparently uselessly, and that in consequence of the trouble which it gives to recognise the mycelium filaments. They go creeping in the intercellular canals, but are so extremely thin and quite colourless, so that they are not to be distinguished from the healthy cell-walls between which they make their way. Only after having got acquainted with the finely granulous contents of the mycelium filaments, by the use of stronger lenses, the task becomes lighter, and when, finally, the cell-walls of the surrounding bark tissue have begun to change colour under the action of the poison, it may be said that the research affords no more difficulty.

Here attention should be drawn to an accidental particularity which, previous to the examination of the diseased Tilia-branches, might well have disappointed our expectations. This, namely, concerned an investigation of diseased branches of *Negundo fraxinifolia* — an ash-tree frequent in gardens — which, by the thickness of the mycelium filaments, the brown tint of their walls, as well as by the presence of transverse partitions, combined with the accompanying nodated appearance in some places, had much more quickly carried us to our end. Under the impression of these observations our research of *Tilia* had begun, and so it was not to be wondered at that at first we thought it much more troublesome to get on, than later it proved in reality to be.

There can be no doubt but the changes, which are observed as

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well in the tissues situated nearer to as in those farther from the mycelium-filaments, and to which belong 1st the decoloration of the bark- and bast-parenchyma-cells, of the phloem-layers, of the medullary rays, and of the wood-parenchyma, and 2nd the killing or liquefaction of those tissues, are caused by the more and more inwardly penetrating mycelium-branches and this in such a sense that by them a substance is secreted — an enzyme — which, as a poison for living plant-cells, exerts a deadly influence upon them. The original contents of the cell grow unrecognisable, and are replaced by a brown-red shapeless precipitate, which proves indifferent to number of reagents (alcohol, ether, kalium chromate, ferrichlorid, caustic kali, ammonia, nitric- and sulphuric acid) and can but be decoloured by a few oxidising substances, as a mixture of kalium bichromate and sulphuric acid, or chromic acid. The poison leaves the bast fibres uncoloured and, in as much as can be ascertained by microscopic observation, unchanged.

In order experimentally to demonstrate the presence of a poisonous substance, Mr. KONING proceeded as follows:

He cut out some hundreds of black spots from young Tilia-bark, crushed them fine under addition of 20 cM^3. of sterilised water and filtered the viscous liquid through a Chamberland-Pasteur-candle. The filtrate amounted to 7 cM^3. and was of a light yellow colour.

With it branches and sections of branches of a healthy *Tilia* were treated; the former by longitudinal incisions with a flamed knife plunged in the liquid, or by injections, the latter by submerging with the liquid in a watch-glass or an experiment tube.

Experiments in both directions with sterilised water and bark sap of healthy Tilia-branches served for control. The result of these proceedings was after 8 days for the incised and injected branches and of 2×24 hours for the sections:

"that what had been treated with sterilised water or with healthy bark sap, had remained uncoloured, but that the wound edges of the incised or injected branches on one hand, and the flat sides of the sections on the other, had suffered a brown, albeit light, colouring".

Another, later performed experiment, quite corresponded with the above described. It concerned some healthy Tilia-branches, cut off with the necessary precautions and of which some were placed in the filtrate of healthy, some in that of diseased Tilia-bark. After 3×24 hours the poison proved, as might be expected, to have most positively exerted its influence, as the original colour of the branches placed in pure liquid, had remained unchanged, whilst that of the

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branches which had been plunged into the infected sap had changed from light brown-red into dark brown.

The perithecia of *Leptosphaeria vagabunda* develop in the bark parenchyma, but gradually they make their way to the surface of the branches where, accordingly, they are then found, like the pycnidia.

The former are much more numerous than the latter and appear either at the surface of the scales, or at the wound edges, or in grooves and cavities. They have solid, black walls and a small ostium, with or without papilla, and contain numerous narrow club-shaped 8 spored asci. Their width or diameter averages from $^1/_5$ to $^1/_2$ mill. The spores are 132 to 154 μ long and 22 μ wide and show so much difference in appearance, according to their age, that one might often be inclined to believe in the existence of two different Pyrenomycetes. By this characteristic *Leptosphaeria vagabunda* is easily recognised among the numerous species of the genus.

In the very youngest period of development the spores are spindle-shaped, colourless and one-celled; somewhat later there appears in their middle a transverse partition; still later the two halves take the form of a very obtuse cone, but which, at a third of its height, appears constricted and then consists of a pulvinate under- and a knob-shaped upperportion; moreover in each of the two portions appear two superposed drops of oil.

Between each two drops now a new partition makes its appearance and accordingly 4, instead of 2 loculaments, are observed. Then the spores again assume their original form, the drops disappear, the deeper constrictions are replaced by superficial ones and the spindle-shape shows itself again. Now, however, the spores have become 4 celled and have got a light olive tint, which both characteristics secure the Fungus its place among the species of *Leptosphaeria* (ibid. *g*).

Notwithstanding the virulence of the poison produced by the mycelium of *Leptosphaeria vagabunda*, which brings about the destruction of an infected branch, nursery-men are not afraid of this parasite, because, according to their experience, the diseased parts are pushed off, and, as they say, the tree outgrows the evil. The justness of this observation is supported by the fact that *Tilia* belongs to the trees which regularly, first in the depth of the bark tissue, afterwards in that of the bast, produce cork-layers which exclude all beyond from the supply of water and thus abandon it to dessication. The thus killed tissue, in which the fungus had nestled, is sooner or later pushed off, or at least rendered harmless, and the absence of stomata and lenticels at the surface of the now

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exposed parts, deprives the spores of every opportunity again to infect the branches.

Besides a few perithicia cut through our figure shows at the outside of the section a pycnidium cut through, i. e. a spore-fruit, in which only free spores are to be seen but none enclosed in asci. This fruit has all the properties of the genus *Phoma*, but was not hitherto distinguished as a species. I call it therefore *Phoma Tiliae* and assign to it the following properties:

PHOMA TILIAE n. sp. Perithecia primo peridermate velata, denique hoc rupto semilibera, subsphaerica, nigra, tandem vertice perforata, 154—225 μ in diam.; sporulae ellipticae, continuae, hyalinae, ad polos rotundatae, $4.5 \times 2.7\ \mu$. Differt a Ph. velata Sacc. et Phoma communi Rob. sporulis enucleatis et multo minoribus ($4.5 \times 2.7\ \mu$ contra $10—12 \times 2.5\ \mu$ et $6—7 \times 1.5$).

This *Phoma* belongs most probably to the cyclus of development of *Leptosphaeria vagabunda*, i. e. is most probably produced by the same mycelium filaments as the ascus-bearing form, but earlier. The proof for this supposition would be procured if from one and the same mycelium both forms of spore-fruits were seen to come forth; or, if from the spores of either form the second was seen to originate, or, lastly, if none of either forms were ever met with separately (unless by high exception), but constantly in company of the other. Hitherto these phenomena could not be stated, so, the last word is not yet said about the relation between the two mentioned forms.

In the course of this paper we have already inferred that the nursery-man does not care for the infection of his lime-trees by *Leptosphaeria vagabunda*, as the diseased parts are thrown off and are not replaced by new ones. Meanwhile it remains advisable to render the infected branches harmless as the ripe spores of both the perithecia and the pycnidia, might afterwards again show their destructive power, and as it cannot be determined beforehand whether the infectious matter might not spread further, than has been observed till now. As to myself, among the thin branchlets, I sometimes met with much thicker ones, which had not a little suffered of the Leptosphaeria-disease.

EXPLANATION OF THE FIGURES.

Plate I. Fig. 1. — Part of transverse section of a one year's lime-tree branch, infected by *Leptosphaeria vagabunda* Sacc.

The colourless spaces α represent the bast-bundles; β brown, in radial

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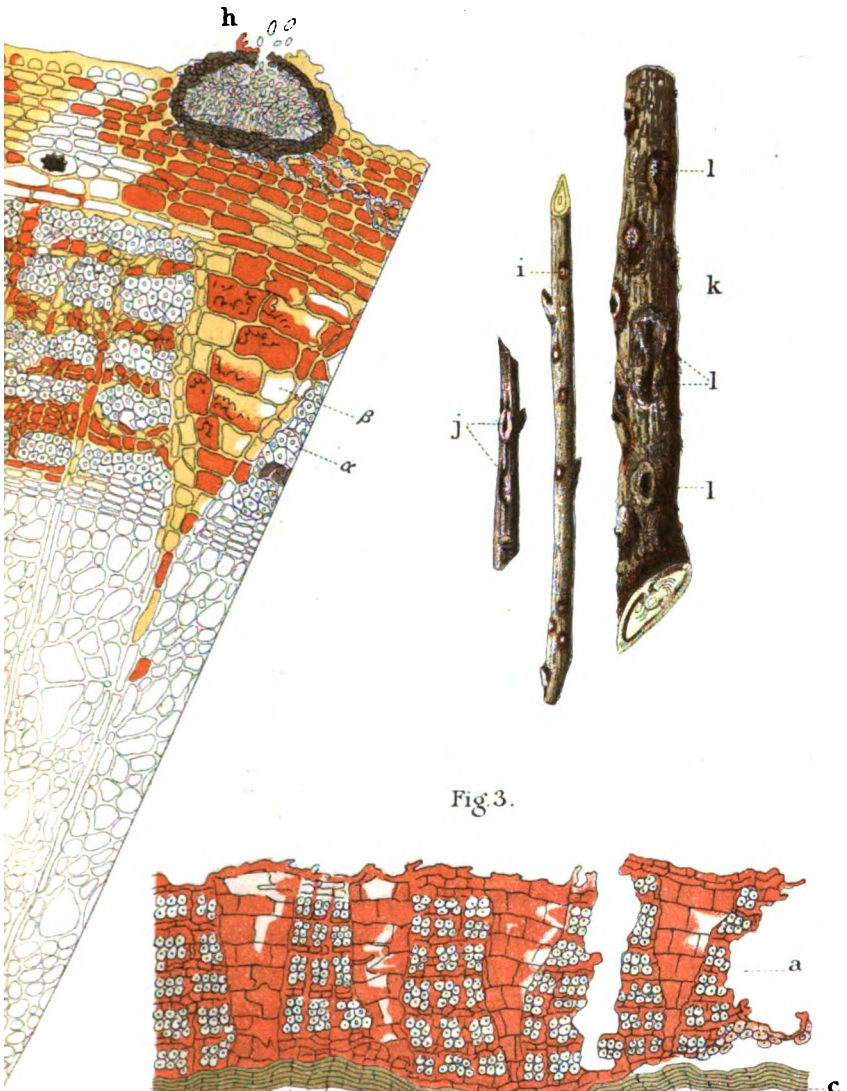
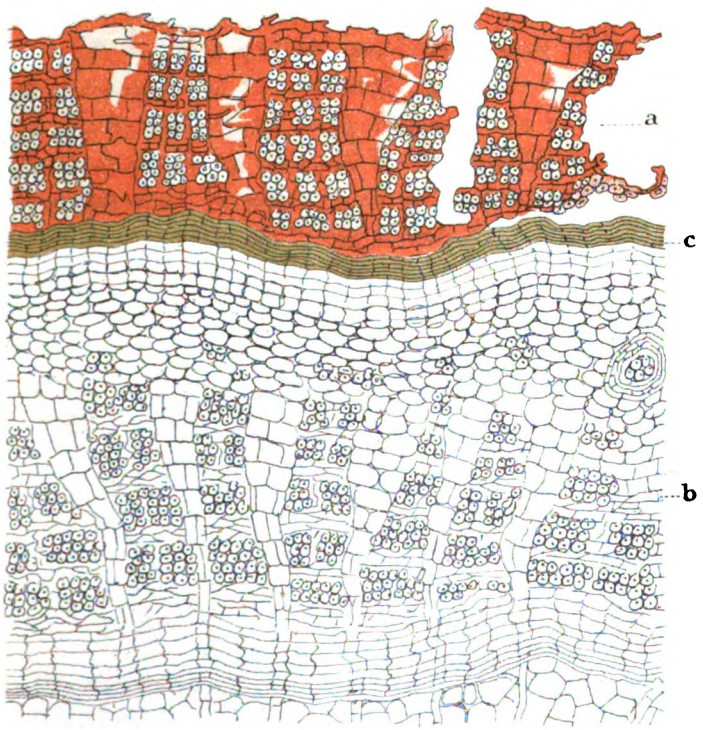


Fig. 3.



J. Eytel, lith. P.J. Mulder, impr. Leiden.

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direction extending medullary rays, of which some upwards fan-shaped elated; γ a fan-shaped elated portion of a medullary ray with a colourless mycelium filament and destroyed tissue.

a. Two perithecia with asci and paraphyses.

b. A perithecium with asci and paraphyses separately.

c. Young ascus.

d. Ripe asci with spores and paraphyses.

e. f. g. Spores of different ages; *e.* and *f.* 2-celled, uncoloured; *g.* 4-celled, coloured.

h. Pycnidium of *Phoma Tiliae* Oud.

i. Branchlet at the beginning of the disease. The black spots with white dot in the middle are distinctly seen.

j. Branchlet in a later period of the disease. Instead of the black spots a scale is seen (the highest) and a wound after the scale is fallen off.

k. Older, knotty branch, upon which some closed perithecia *(l)*.

m. Lenticel, out of which a mycelium filament has penetrated more deeply and has occasioned decolouring of the bark-parenchyma cells and destruction of tissue.

Fig. 8. Piece of lime-tree bark cut transversely to show the detaching of a diseased part (*a*) from the still healthy, more profoundly situated (*b*) portion. At *c* the cork layer is seen which has brought about the separation between diseased and healthy tissue.

c. Hyalophragmiae.

5. METASPHAERIA TAXI Oud. n. sp. On the leaves of *Taxus baccata*. — Nunspeet, 18 Sept. 1898; Mr. BEINS. — Perithecia epigena, valde numerosa, gregaria, $^1/_8 - ^1/_6$ mill. in diam., continuo sub epidermide abscondita, tandem prominentia, vertice perforata, nigra, carbonisata, applanato-globulosa; asci claviformes, saepe curvati, $65 - 70 \times 9 - 10$ μ, paraphysibus filiformibus obvallati; sporae 8, distichae, colore destitutae, lanceolatae vel obovato-lanceolatae, 3-septatae, ad septa non constrictae, $18 - 23 \times 4^2/_3 - 5^1/_2$ μ.

d. Dictyosporae.

6. PLEOSPORA NEGUNDINIS Oud. — On the one- to three years' branches of *Negundo fraxinifolia* and *californica*, often in company of *Phoma Negundinis* Oud. — March, 1900. Bussum, and elsewhere in „het Gooi". — Mr. C. J. KONING.

Ramicola. Perithecia gregaria, primo epidermate vel peridermate tumidulo velata, postea papilla apicali, postremo toto corpore exposita, globoso-depressa, $^1/_3 - ^1/_2$ mill. in diam., papillata, nigra, glabra, contextu parenchymatico, fuligineo. Asci cylindracei vel cylindraceo-clavati, subsessiles, vertice rotundati, $120 - 176 \times 22 - 23$ μ, paraphysibus paullo longioribus obvallati, octospori. Sporidia disticha, oblonga, medio leniter constricta, utrimque rotundata, $25 - 35 \times$

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12—16 μ, primo hyalina, 1-septata, mox flavescentia, 3- et 5-, postremo mellea, 7-septata, atque, loculamentis interseptalibus fere omnibus septis 1 vel 2 longitudinaliter denuo divisis, muriformia. A *Pleospora Gilletiana* Sacc. (Fgi ital. del. tab. 330 et Berlese Icon. Fung. vol. II, fasc. 1, tab. XX f. 2) differt ascis latioribus (23 μ contra 14—15 μ), sporidiis distichis neque monostichis, rectis neque curvatis; absentia hypharum basilarium expositarum.

The above described fungus causes much damage to the plants which it attacks and destroys, and loss to the cultivator. According to informations obligingly afforded to Mr. KONING by Mr. JAC. SMITS, nursery-man at Naarden, the phenomena of the disease manifested themselves for the first time in 1898, on plants, cultivated on soil, deprived of sand. On argillaceous and sandy soils they were not observed as yet. In most cases, the variegated specimens of *Negundo* have much to suffer, though, as an exception to the rule, it is worth mentioning that in the nursery of Mr. VERSTEGEN at Naarden, p.m. 500 M. distant from that of Mr. SMITS, specimens of *Negundo californica*, with purely green leaves, were attacked by our *Pleospora*. On the var. *Kosteriana* of *N. fraxinifolia*, and on the aurated variety of the latter, the disease was not seen hitherto.

On branches, older than three years, the *Pleospora* does not occur. The nusery-man is usually not aware of the disease before St. John (21st June), which does not prevent, however, that in September ensuing many may be dead already.

Pleospora Negundinis Oud. and *Phoma Negunndinis* Oud. seem genetically to belong to each other. Usually they are found on the same branch (Pl. I, Fig. 2 *d* and *a* and Fig. *k*, *l* and *m*) and in each other's vicinity, in which case the perithecia of the former are recognised by their larger dimensions and looser dispersion, those of the latter by their smaller dimensions and more compact crowding.

The perithecia of *Pleospora Negundinis* are concealed in the bark-parenchyma, but with dried twigs, by the shrinking of the softer parts, they seem to repose on the bast-bundles. At their foot, hidden in the parenchyma, are seen numerous brownish mycelium filaments which spread around and ramificate (*d*). In our figures is seen under the same circumstances a *Phoma*-pycnidium (*a*) and a bundle of brown, upright filaments (*b*) of a black mould, all supported by hidden mycelium-hyphae, which cannot be distinguished from those of the *Pleospora*-perithecia. These filaments, like those of *Leptosphaeria*, secrete a poison, and cause a modification, though apparently not equally important, of the contents of the parenchymacells of the bark and of those, situated in the direction of the medullary

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rays. The diseased spots (*h*) grow, at the surface of the branches, from green to red-brown, over larger or smaller extents, in accordance with the bark-parenchyma, situated under the epidermis which, however, though likewise red-brown, keeps a lighter tint. If a branchlet, spotted by the disease, dies (*h*), the red-brown colour turns of a gray one, though the tint of the mycelium continues unchanged, and on the sharply marked spots the perithecia, often preceded by pycnidia, are seen to appear. On the drawing, the red-brown tint is not represented, for the very reason that it was borrowed from a dead branchlet. Some cells — those containing chlorophyll — have till now escaped the influence of the poison.

Tissue-elements of an abnormal colour frequently appear in *Negundo* at places where no myceliumfilaments are found. Bast- and phloem-bundles seem to resist the influence of the poison.

The largest *Pleopospora*-perithecia are found at the oldest internodes, so that it seems not doubtful but these organisms require much time for their complete development. In accordance with this is the fact, that the larger perithecia may quite have thrown off the periderma above them, while with the smaller and younger ones this protecting layer is still extant and is only perforated by the papilla perithecii.

Of destructions in the shape of resorption of tissues and the appearance of caverns, quite differently from *Leptosphaeria vagabunda* on *Tilia*, nothing is observed. Notwithstanding this the poisonous power of the *Negundo*-fungus is much more vigorous than that of the *Tilia*-fungus, as is proved by the fact, that, according to the experience of nursery-men, the once infected *Negundines* are vowed to death, while the *Tilias*, as they say, overgrow the evil and persist.

The disease of the Negundo-branches is, as in *Tilia*, announced by local decolorations of the cork-tissue, upon which first red-brown, and later paled, black-encircled dots become visible. By-and-by the said dots begin to wrinkle and to detach from the lower bark parenchyma. Meanwhile tiny, black, corpusculae appear through the peridermis and gradually increase so much in height as to attain this membrane. By the pression which they exert on it the surface of the branchlet grows somewhat uneven, until the papillae of the perithecia perforate the periderma. In this state the asci and spores, which had been introduced into the inside of the perithecia, have not yet attained their full growth. Only when their diameter is increased to about $^1/_2$ mill. these organs are not sought in vain, so that then a commencement can be made with their de-

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scription and measurement. As we formerly inferred already, the ripe spores sometimes are oblong-elliptical, sometimes club-shaped, and have a yellow or yellow-brown colour. In well-developed specimens are found 7 partitions and a superficial constriction on a third of their height. Usually the foremost half, i.e. the one turned to the summit of the ascus, is a little wider than the backpart. Each loculament is divided by one or two longitudinal partitions, into smaller ones, so that the whole bears some resemblance to a brick wall, whence the expressions: "Sporae muriformes", "Spores muriformes", "Spores murées", "muriform spores". There are spores whose longitudinal partitions lie in each other's direction and together form a straight line, but there are others where 1 and 2 partitions alternate in the successive loculaments.

The infection in *Negundo* does not occur through interference of stomata, but probably through that of wounds, found near the foot of the leaf-buds, and without doubt caused by tensions during the growth. There at least are commonly found the first abnormally coloured spots. Other places are not excluded, probably, however, wounds will there, too, have given access to the spores.

If we survey the results to which have led the investigation of the *Tilia-* and *Negundo*-diseases, we find that they agree in so far as:

1st. they are caused by Pyrenomycetes: the *Tilia*-disease by *Leptosphaeria vagabunda*, the *Negundo*-disease by *Pleospora Negundinis*;

2nd. in both often lower fruit-forms, such as one or more kinds of pycnidia and *Dematieae*, precede the perithecia;

3rd. in both, not the fruits (perithecia or pycnidia), but the mycelium-filaments are the producers of the evil;

4th. in both by these filaments a poison is secreted, which in *Tilia* — and most probably also in *Negundo* — persists in its action, even after filtering through a Chamberland-Pasteur-candle, so, deprived of all solid components, and that consequently in both cases the nearest cause of the disease of the plantcells must be ascribed to the action of an enzyme;

5th. in both cases the same portion of the bark (the parenchyma) is affected, and the phloem-fasciculae seem beyond the noxious influence of the mycelium-filaments.

Both diseases, on the other hand, differ from each other, in as much as:

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1st. the mycelium-filaments of the *Tilia*-disease are colourless, devoid of partitions, very thin and delicate and so not easily perceived, while those of the *Negundo*-disease unite a brownish tint with the possession of partitions and a great solidity, and accordingly attract more the attention;

2nd. the volume of all the mycelium filaments jointly, when compared to the space in which they are spread, is much smaller for *Tilia* than for *Negundo*;

3rd. the enzyme of the *Tilia*-disease acts more locally, that of *Negundo* also at a distance; the former can give rise to liquefaction of tissue, the latter not.

EXPLANATION OF THE FIGURES.

Plate I, fig. 2. — Portion of a transverse section of a one year's branch of *Negundo fraxinifolia* (Acer Negundo), attacked by *Pleospora Negundinis* Oud.

a. Pycnidium with *Phoma Negundinis* Oud.
a'. The same, separately.
b. A bundle of unripe hyphae of a Dematiea.
c. Coloured mycelium.
d. Perithecium.
d'. The same, magnified.
e. Ripe asci.
f. Paraphyses.
g. Mycelium.
f'. Spores.
h. A dying more-years' branchlet.
i. Dying brown fragment of bark.
j. Dead colourless fragment of bark.
k. Dead branchlet.
l. Perithecia with asci.
m. Pycnidia of Phoma.

SCLEROPLEA n. g.

Genus Pyrenomycetum e familia Sphaeriacearum et e sectione Dictyosporarum, generi „Pleospora" proximum, tamen ab eo distinctum perithecio duplici: uno nempe interiore (spurio) tenuiore, incompleto (i.e. sursum hiante), e cellulis rotundatis composito, ascos sporigeros et paraphyses fovente; altero exteriore (vero) crassiore, magis resistente, nigro, carbonaceo, strato parenchymatoso hyalino, satis voluminoso, a priore distincto.

7. Scleroplea Cliviae n. sp. — Perithecia innato-erumpentia, subgregaria, sphaerico-depressa, calva, 0.5 mill. in diam., summo apice tantum supra epidermidem prominentia et coriaceo-carbonacea; asci cylindraceo-subclavati, in pedicellum brevem et crassum abrupte

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desinentia, octospora, 100—140 × 15—35 μ, paraphysibus longioribus articulatis obvallati; sporae distichae, fulvo-flavescentes, elliptico-obovatae, utrimque obtusissime rotundatae, muriformes, 7-, rarius 6-septatae, loculis interseptalibus omnibus, ultimis tantum vulgo exceptis, septis 1 vel 2 longitudinaliter divisae, ad septum medium constrictae, parte dimidia anteriore parum tumidiore, 35×10 — 12 μ; paraphyses ascis paullo longiores, articulatae.

On the leaves of cultivated specimens of *Clivia nobilis*. December 1899. Hees near Nijmegen.

In the Meeting of the section of 28 November 1896, a paper was presented by me, entitled: "Notice sur quelques "Champignons nouveaux", which was published the 9th December of the same year in the Proceedings of the Meeting. To the still unknown Fungi, discussed in this paper, belonged also *Chaetostroma Cliviae*, of which on pag. 226 of the said Proceedings an accurate description is found.

The plant, attacked by *Chaetostroma* was the well known *Clivia nobilis*, and the diseased specimen, sent me by Professor Dr. J. RITSEMA BOS, grown in the garden of Mr. GERRITSEN, at Hees, near Nijmegen.

Having after the 28th of November 1896 heard nothing more of diseased *Clivia*-leaves, I received, on the 27th December 1899, accompanied by a letter from Mr. C. J. J. VAN HALL, Candidate in Botanics and Zoology and assistant to Prof. RITSEMA BOS, in Amsterdam, some *Clivia*-leaves from the same garden, again diseased by *Chaetostroma Cliviae*, but moreover provided with perithecia with ripe asci and spores, which latter, by reason of their well-known characteristic structure, were recognized by Mr. VAN HALL as *Pleospora*-spores.

The diseased leaves looked like fig. 4 on Plate II. At their upper face, markedly separated by a dark line, could continually be distinguished two portions, of which only the smaller foremost one was beset with groups of perithecia, the larger back portion, on the contrary, was wholly devoid of these black points. The purely green colour of before was no more to be observed at the back portion, but it was replaced by a yellow or yellowish dingy one, whose equality had come forth from the confluence of primitively smaller, later more increased spots. At the foremost, perithecium-bearing portion, the change of green into yellow had never been observed, but instead a decrease in freshness of the green, combined with the appearance of a brown tint, and corresponding with that a drying and withering, so that it might be said that quite ripe perithecia were observed exclusively at the withered summits of the leaves. As afore mentioned, the *Cheatostroma*-pustulae occurred indeed on the yellow portions of the leaf, but then the withered

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portions were wanting there and the dark line proved to be the demarcation, not between gray-brown, withered perithecium-bearing, and green or stained unfertile parts, but between yellow, perithecium-bearing and green unfertile parts.

A vertical section of *Chaetostroma Cliviae* (Pl. II fig. 2) gives an idea of the structure of this fungus of which in our former paper only a conidium, supported by its basidium, was figured (Pl. II, fig. 3). The intact fungus, 25 times magnified, is seen on Pl. II, fig. 1.

The fungus allied to the genus Pleospora as regards its spores is, 25 times magnified, represented on Pl. III, fig. 2. In the leaf-parenchyma, arrived at its full growth, it tries to perforate the epidermis of the leaf, in which it succeeds at last. As is seen, this protective layer is hereby pushed asunder, sometimes into 3 lip-shaped slips.

A vertical section of the perithecium and its environment is figured on Pl. II, fig. 5. Here the remarkable fact presents itself that the true perithecium (*a*) does not directly surround the so-called nucleus (asci and paraphyses) but is separated from it by a wide layer of parenchyma-tissue (*c*), and besides, by a pseudo-perithecium wall. The question whether this special condition of which no other instance was known to us among the singular dictyosporic Pyrenomycetes, had perhaps been observed by other mycologues, called forth a nearer investigation, and so we found that already SACCARDO had in some way alluded to it on p. 277 of Vol. II of his Sylloge, where the 3rd sub-division of the genus *Pleospora*, named "Scleroplea", is being discussed.

SACCARDO, namely, divided the numerous species of *Pleospora* into three categories:

I. *Eu-Pleospora.*
II. *Catharinia.*
III. *Scleroplea.*

Of these the 1st (p. 241) embraces the species with thin-walled, membranous perithecia and coloured spores;

the 2nd (p. 275) the species with thin-walled (membranous) perithecia and colourless spores, and finally;

the 3rd (p. 277) the species with thick-walled perithecia, and coloured spores.

Eu-Pleospora embraces the most numerous, and long since known, species, always indicated by the simple name of *Pleospora*; whilst to *Catharinia* are assigned no more than eight, and to *Scleroplea* only two species. Nevertheless *Catharinia* was in 1896 by SACCARDO

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in Vol. XI of his Sylloge, and in 1897, independently of SACCARDO, by myself in Vol. II of my "Révision des Champignons des Pays-Bas", raised from a sub-genus to an independent one.

With a view to the above diagnoses there was no doubt but the *Pleospora* produced by *Clivia* must belong to *Scleroplea*, as both characteristics: a thick, as carbonised wall, and coloured spores, were present.

The question now presented itself whether, now that *Catharinia* had been raised to an independent genus, the same measure should not be applied to *Scleroplea* too. It appeared to us that no motivated doubt could thereabout exist for the following reason: not only because a thick, as carbonised, opaque perithecium-wall might be called as great an exception among the *Pleospora*-species as the colourless spores of *Catharinia*, but also as the structure of the perithecia, as we have seen, is of a much more complicated nature than that found in the species of *Eu-Pleospora* and *Catharinia*.

Cause of astonishment might be found in SACCARDO's not recording among the characteristics of his sub-genus the by us observed special structure of the perithecia of *Scleroplea*, yet the reason of this lies at hand. The two species of *Pleospora* which are noted in the Sylloge under the afore-mentioned sub-genus, having selected for their dwelling-place the organs of exotic plants, flourishing in New-Zealand and Argentinia, were not, or only in dried state examined by him, so that he had to depend on the descriptions of others, who had, perhaps, likewise, worked under unfavorable circumstances, or whose attention had not by preference been directed to the internal structure of the perithecia.

Only for *Pleospora nuda* (Sac. Syll. II, 277 = Pyrenophora nuda Cooke, Grevillea VIII, 68) — called by COOKE "nuda", because he was of opinion that in this fungus no perithecium had come to development, SACCARDO alludes to the phenomenon observed by us, using the following expressions: "Secundum COOKE stratum perithecii exterius brunneo-cellulosum a perithecio vero interiore separabile est."

Meanwhile it should be borne in mind that COOKE who wrote in English, did not use the terms attributed to him by SACCARDO, but simply asserted: "These are no true perithecia. The cells surrounding the perithecial cavity are brown, globose and readily separable". SACCARDO has consequently wrongly understood COOKE's words, but still, at least as regards *Scleroplea Cliviae*, has come very near the truth. How much, however, the views of both mycologues diverge, is obvious to any-one who pays attention to the fact that COOKE disowns the existence of a true perithecium, whilst SACCARDO, on the con-

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trary, infers the presense of two perithecia, and that the English mycologue does not recognise our layer (*d*) as a perithecium-wall, whilst the Italian savant applies to it the name of "perithecium interius".

But let us leave to both authors the responsibility for their respective judgments and exclusively consider the results of our microscopic investigation most successfully reproduced by Mr. VAN HALL in Fig. 5 on Plate II, we then come to the conclusion that the perithecia of *Scleroplea Cliviae* are built up of:

1st a thick, solid, as carbonised black layer of cells (*a*) (the "stratum perithecii externum" of SACCARDO; probably the continuation downward and inward of the "cuticula nigrefacta" of COOKE;

2nd a many cells thick layer of thin-walled parenchyma built up of polyhedral elements (*c*);

3rd an imperfect, i.e. at the upperside not closed layer of light brown globose cells (*d*) surrounding the nucleus perithecii, that is to say the asci and paraphyses ("the brown and easily separable cells, surrounding the perithecial cavity" of COOKE; "perithecium interius" of SACCARDO);

and that the raising of the sub-genus *Scleroplea*, to a genus chiefly reposes with us on the presence of an external and internal perithecium, separated from each other by a rather vigorously developed interpushed parenchyma which, at a later period, probably passes into decay and in doing so breaks up the connection between the said two layers.

If we admit, — which however ought to be determined by a nearer research, — that *Pleospora nuda* SACC. (= Pyrenophora nuda COOKE) and *Pleospora sclerotioides* correspond with *Scleroplea Cliviae* in the structure of their perithecium, then the latter genus, to be interposed between *Pleospora* and *Pyrenophora*, would for the present moment consist of 3 species, all bound to exotic plants.

By the addition of iodium the ascus-wall of Scleroplea Cliviae assumes a red-brown (presence of glycogene), the spore-wall a blue-green, and the contents of the spores a blue colour.

The germination of the spores, tried by Mr. VAN HALL in a decoction of Clivia-leaves, was satisfactory. After the separate spores were strongly swollen, many began to send out germinal tubes. (Plate III, fig. 5.)

The question whether *Chaetostroma Cliviae* and *Scleroplea Cliviae* are to be considered either as parasites or as saphrophytes, should, we think, be answered in the latter sense, because in the tissue of

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the faded yellow leaves or parts of leaves, where no black spots appear, no trace of mycelium filaments is to be found [1]). The decoloration, the cause of which remained unknown to us, precedes accordingly the appearance of the fungus.

An effort was made by Mr. VAN HALL to infect a dying Clivia-leaf with ascospores of Scleroplea in state of germination. The result of the experiment was not favorable. Small black points developed indeed in the environment of the inflicted wound, but they soon ceased growing, so that it remains undecided whether they belonged or not to *Chaetostroma*.

EXPLANATION OF THE FIGURES.

Plate II, fig. 4. A leaf infected by *Scleroplea Cliviae*. The foremost brown portion bears small groups of perithecia, of which the summits are only visible. The hindmost yellow portion bears neither of the two fungi and contains no mycelium filaments.

Fig. 2. Vertical section of a pustula of *Chaetostroma Cliviae* Oud., described more in details on pag. 226 of the Proceedings of the Meeting of 28 Nov. 1896.

Fig. 1. Some *Chaetostroma* pustulae 25 times magnified. The chaetae to which the genus owes its name, can be distinctly seen.

Fig. 3. A conidium of *Chaetostroma Cliviae*, reposing on its basidium, 500 times magnified.

Fig. 5. Vertical section of a perithecium of *Scleroplea Cliviae* (216 times magnified).

a. exterior or primary perithecium.

d. interior or secundary perithecium.

c. parenchyma tissue between the primary and secundary perithecium.

b. asci.

Plate III, fig. 1. Older and younger perithecia of *Scleroplea Cliviae* (8 times magnified).

Fig. 2. Some perithecia of the same, which have torn asunder the epidermis (25 times magnified).

Fig. 5. Spore of the same in state of germination.

Fig. 3. Spore-bearing ascus with its paraphyses (800 times magnified).

Eig. 4. Four spores of different ages and sizes of the same (800 times magnified); *a. a. a.* moistened spores, *b.* spores soaked in water.

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[1]) At our request Prof. P. MAGNUS in Berlin had the kindness to test the accuracy of our research with some leaves sent to him; he fully confirmed it.

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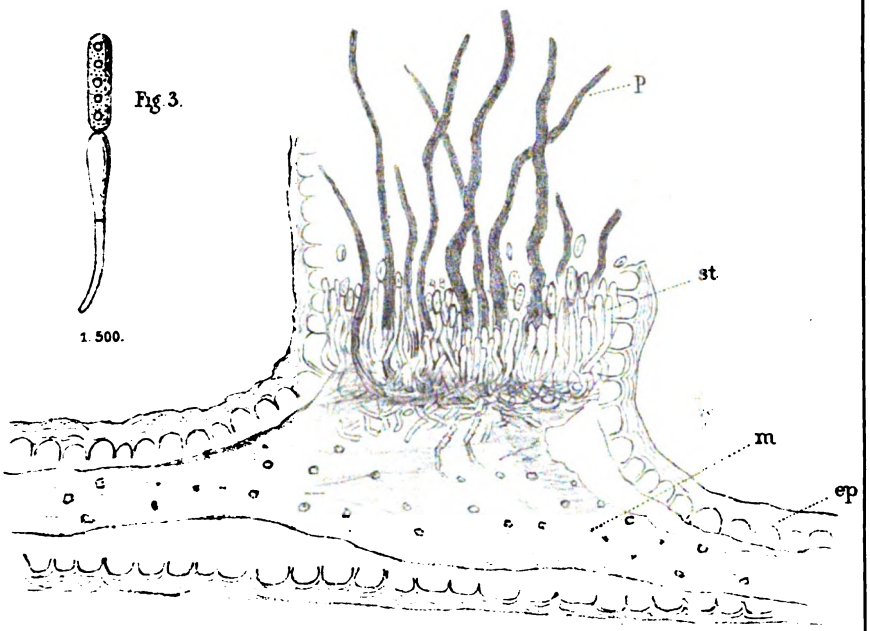
Fig. 2.



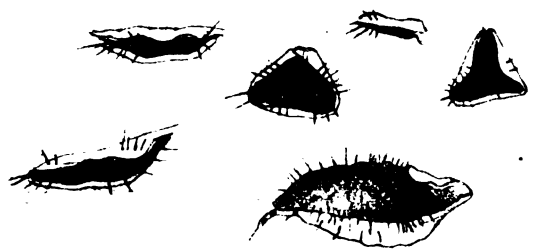


Fig. 5.

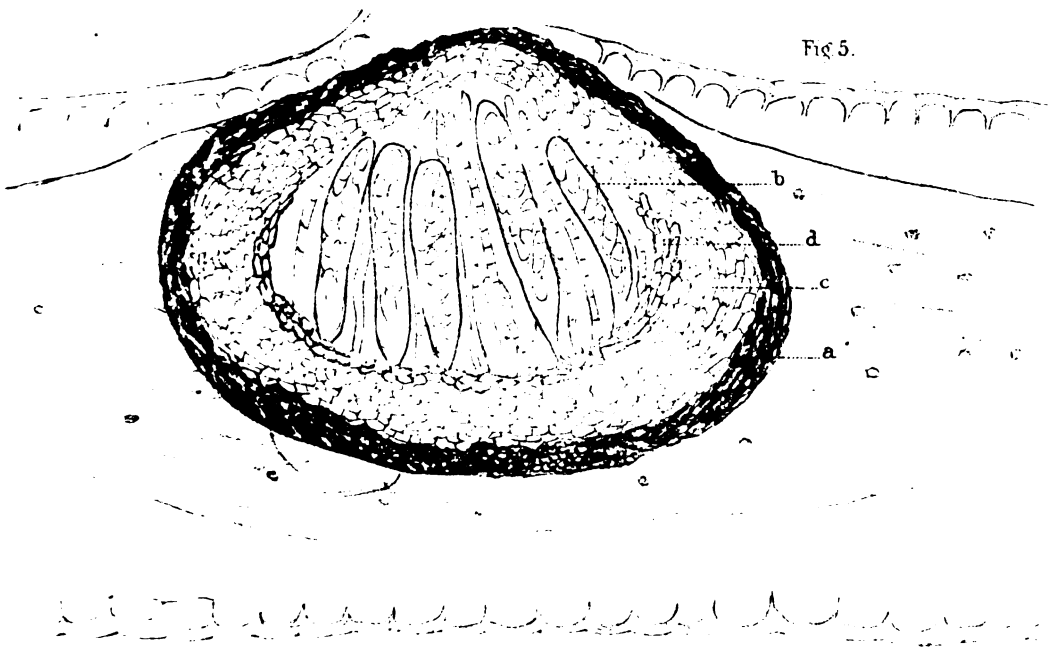


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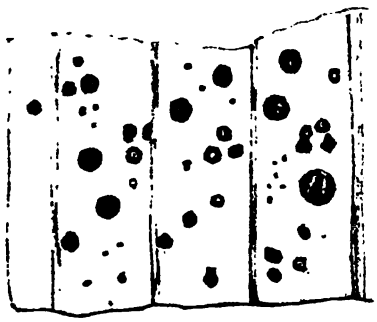
Fig. 1.



1:8.

Fig. 2.

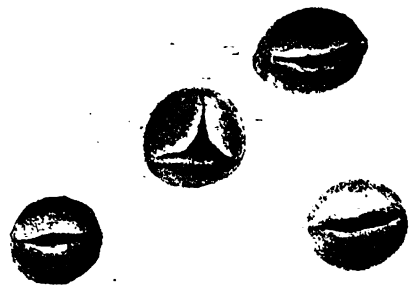


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Fig. 5.

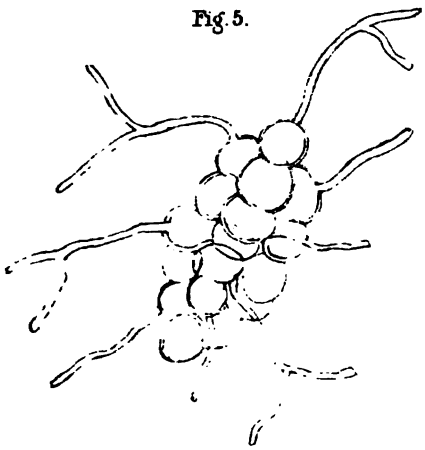

Fig. 3.

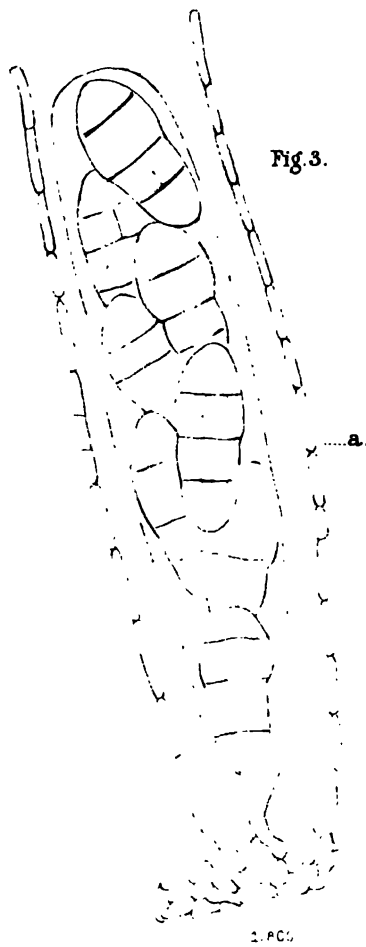

Fig. 4.

1:800.

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Astronomy. — "*The motion of the Pole of the Earth according to the observations of the last years*". By Dr. E. F. VAN DE SANDE BAKHUYZEN.

In a postscript to my last paper on the motion of the pole of the earth in "*Archives Neérlandaises. Série II, Tome II*" I briefly mentioned in how far the results from the latest observations deduced by ALBRECHT in his "*Bericht am Schlusse des Jahres* 1898", agreed with my formulae.

Since that time Prof. ALBRECHT has again published in a following paper [1]) his summaries and calculations including one year more. This closes in a certain sense a period in the researches of our problem. Up to 1899 the results obtained were due to the free co-operation of a certain number of observatories. At the close of 1899 however, the new international organisation has come into force, according to which observations after the Horrebow-method are made in exactly the same way in six stations which all are situated on 39°8′ northern latitude, and have been especially arranged for this purpose.

Therefore this seemed to me the proper moment for making a new comparison between my formulae and the results deduced by ALBRECHT from the combined observations of the last 10 years.

2. ALBRECHT takes the results obtained in his "*Bericht im December* 1897" to be definitive for the period 1890—1895.0. In his last "*Bericht*" therefore he considers only the period from 1895.0—1899.8, for which he had at his disposal the results of on the whole the same observatories as before.

For the intended comparison I chose for the 14-monthly motion my elements II of *Archiv. Neérl.* T. II, p. 481 (35), for the yearly motion my results derived from the period 1890—96 (*Proc. Royal Academy of Amsterdam*, June 1898).

Here follow the results of this comparison. The differences between the observation and the computation are expressed in thousandths of seconds.

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[1]) TH. ALBRECHT, Bericht über den Stand der Erforschung der Breitenvariation am Schlusse des Jahres 1899. Berlin 1900.

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x ALBRECHT — x computed.

	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
1890	— 93	— 48	— 3	+ 29	+ 22	+ 22	+ 6	— 32	— 75	— 88
91	— 90	— 36	+ 6	+ 20	+ 50	+ 44	+ 17	+ 1	+ 6	+ 29
92	+ 46	+ 49	+ 2	— 23	— 43	+ 21	+ 43	+ 29	— 10	— 29
93	— 20	— 9	+ 8	+ 14	+ 3	+ 41	+ 20	+ 6	— 2	+ 6
94	+ 18	+ 34	+ 50	+ 56	+ 22	+ 9	— 5	— 8	+ 9	+ 42
95	+ 49	+ 19	— 26	— 70	— 85	— 63	— 15	— 17	— 4	+ 18
96	+ 44	+ 50	+ 22	— 11	— 44	— 44	— 36	— 19	+ 8	+ 42
97	+ 65	+ 58	+ 22	— 21	— 59	— 77	— 84	— 66	+ 7	+ 53
98	+ 113	+ 130	+ 95	+ 52	— 15	— 89	— 103	— 72	— 55	— 46
99	+ 11	+ 81	+ 130	+ 150	+ 123	+ 20	— 69	— 109	— 98	

y ALBRECHT — y computed.

	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
1890	— 26	+ 55	+ 90	+ 70	+ 24	+ 4	— 25	— 27	— 28	— 47
91	— 54	— 13	+ 23	+ 74	+ 41	— 38	— 100	— 125	— 74	+ 5
92	+ 70	+ 91	+ 33	— 29	— 75	— 2	+ 36	+ 45	0	— 13
93	— 8	+ 11	+ 10	— 10	— 22	+ 9	— 11	— 5	— 5	— 19
94	— 15	— 12	+ 16	+ 49	+ 17	+ 6	— 4	— 6	0	+ 4
95	— 14	— 7	— 20	— 32	— 26	— 21	+ 41	+ 50	+ 42	+ 10
96	— 5	— 22	— 43	— 36	+ 5	+ 56	+ 64	+ 58	— 8	— 2
97	— 6	— 28	— 42	— 61	— 42	— 2	+ 71	+ 127	+ 169	+ 88
98	+ 59	+ 26	— 36	— 85	— 93	— 60	+ 7	+ 56	+ 87	+ 87
99	+ 72	+ 23	— 14	— 52	— 67	— 64	— 23	+ 3	+ 28	

From this we find as mean value of the deviations:

$$\sqrt{\frac{\Sigma \Delta x^2}{n}} = \pm 0'',054 \qquad \sqrt{\frac{\Sigma \Delta y^2}{n}} = \pm 0''.050.$$

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or if we omit the results for 1899.0—1899.8 as being probably less accurate as yet:

$$\sqrt{\frac{\Sigma \Delta x^2}{n}} = \pm 0''.047 \qquad \sqrt{\frac{\Sigma \Delta y^2}{n}} = \pm 0''.050.$$

Formerly the mean deviation was found to be $\pm 0''.040$ and $\pm 0.''045$, and we see that the agreement has not improved during the last years.

The fact, that this time I did not use for the 14-monthly motion the results obtained from the period under consideration only, may have slightly increased the deviations, but at any rate its influence cannot have been great.

3. First of all we had now to investigate whether the agreement might be improved by deducing for the whole period new elements for the yearly motion, although it was improbable that this would have much influence.

For this deduction, we have started from the above-mentioned differences, obs.—comp. and have derived from them the corrections of the elements formerly assumed. The values since 1899.0 were not considered and the results of the 9 years 1890.0—1898.9 were combined to 10 mean values in the same way as before.

In this way we found for the components of the yearly motion the following revised values:

$$x = + 0''.100 \cos 2\pi \frac{t-270}{365} \qquad y = + 0''.054 \cos 2\pi \frac{t-148}{365}$$

and hence again:

Position-angle Maj. axis ellipse 19° east of merid. of Greenw.

Components of the motion in the direction of the principal axes:

$$x' = + 0''.104 \cos 2\pi \frac{t-Oct.\ 5}{365} \qquad y' = - 0''.044 \sin 2\pi \frac{t-Oct.\ 5}{365}$$

and so the results are but slightly different from those found formerly.

The variations, which the computed co-ordinates (on the original axes) for the 10 starting-points have undergone, together with the differences, obs.—comp., follow here:

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Δx comp.	$O-C.$	Δy comp.	$O-C.$
+ 0″018	— 0″003	+ 0″007	— 0″007
+ 22	+ 05	— 01	+ 12
+ 19	+ 01	— 09	+ 13
+ 08	— 03	— 14	+ 07
— 06	— 10	— 13	— 06
— 18	+ 03	— 07	+ 02
— 22	+ 05	+ 01	+ 08
— 19	— 01	+ 09	+ 10
— 08	— 05	+ 14	+ 06
+ 06	— 03	+ 13	00

If now again we derive the mean values of the residual differences O.—C. for ALBRECHT's original co-ordinates, we find:

from the 99 values from 1890.0—1899.8

$$\sqrt{\frac{\Sigma \Delta x^2}{n}} = \pm 0''.050 \qquad \sqrt{\frac{\Sigma \Delta y^2}{n}} = \pm 0''.048$$

from the 90 values from 1890.0—1898.9

$$\sqrt{\frac{\Sigma \Delta x^2}{n}} = \pm 0''.045 \qquad \sqrt{\frac{\Sigma \Delta y^2}{n}} = \pm 0''.049$$

As will be seen, the mean value of the deviations still remains greater than that formerly found for the years 1890—1897, and the deviations for the last years still show a very distinct systematic character. Therefore, although the possibility remains that the systematic errors have a greater influence than might be anticipated, it becomes probable that the true motion of the pole deviates even now perceptibly from my simple formula.

If this is the case, we can make 3 suppositions:

1 the yearly motion is more complicate than was assumed;

2 the elements of the 14-monthly motion are not constant;

3 there are still other partial motions besides the two mentioned.

Any observed motion may be explained *mathematically* in any of the three suppositions, and then it remains only to be seen which of these will lead to the *physically* simplest explanation.

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Probably a long series of accurate observations will still have to be made before a decision on this matter can be taken. Yet, in order to prepare later researches in this direction, I have considered to which conclusions the material in hand would lead *in the first two suppositions.*

4. In the first place I have supposed that the assumed 14-monthly motion is correct, and that its elements are constant. Assuming this I have investigated which yearly motion would be found for the three periods: 1890—1892, 1893—1895 and 1896—1898 successively.

The following results were obtained:

1890—1892.

$$x = + 0''.118 \cos 2\pi \frac{t - 247}{365} \qquad y = + 0''.092 \cos 2\pi \frac{t - 117}{365}$$

1893—1895.

$$x = + 0''.113 \cos 2\pi \frac{t - 268}{365} \qquad y = + 0''.065 \cos 2\pi \frac{t - 149}{365}$$

1896—1898.

$$x = + 0''.090 \cos 2\pi \frac{t - 302}{365} \qquad y = + 0''.047 \cos 2\pi \frac{t - 217}{365}$$

and hence I derived:

Position-angles with respect to the merid. of Greenwich:

1890—1892	Major axis ellipse			34° east.
1893—1895	„	„	„	19° east.
1896—1898	„	„	„	4° west.

Components of the motion in the direction of the principal axes:

1890—1892.

$$x' = + 0''.135 \cos 2\pi \frac{t - \textit{Sept.}\ 21}{365} \qquad y' = - 0''.063 \sin 2\pi \frac{t - \textit{Sept.}\ 21}{365}$$

1893—1895.

$$x' = + 0''.119 \cos 2\pi \frac{t - \textit{Oct.}\ 5}{365} \qquad y' = - 0''.055 \sin 2\pi \frac{t - \textit{Oct.}\ 5}{365}$$

1896—1898.

$$x' = + 0''.090 \cos 2\pi \frac{t - \textit{Oct.}\ 27}{365} \qquad y' = - 0''.047 \sin 2\pi \frac{t - \textit{Oct.}\ 27}{365}$$

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If the differences between these results are not to be ascribed to perturbing influences during the observations (for instance local refractions), our first supposition would lead us to the conclusion that the elements of the yearly motion have varied gradually. The pole would have remained behind in its motion, or actually would have described its orbit in more than a year, while the orbit itself would have become smaller, and the apses of the ellipse would have moved in a direction opposite to that of the pole itself [1]).

5. After this I have started from the second supposition. The yearly motion was taken to be constant, and first I assumed for it the elements, which had been derived sub 3. Assuming this the 14-monthly motion was derived separately for the same 3-yearly periods as have been considered sub 4.

The results obtained were:

	Amplitude.		Corr. Epoch.	
	from x	from y	from x	from y
1890—1892	0″188	0″175	— 12 d.	— 11 d.
1893—1895	0.131	0.138	— 2	— 2
1896—1898	0.119	0.132	+ 24	+ 28

Secondly I assumed the yearly motion to be as it had been derived formerly from the observations 1890—1896, and then made the computation again in the same way.

This time the results were:

	Amplitude.		Corr. Epoch.	
	from x	from y	from x	from y
1890—1892	0″173	0″168	— 9 d.	— 8 d.
1893—1895	0.146	0.146	— 4	— 4
1896—1898	0.105	0.126	+ 29	+ 32

differing but slightly from those of the first computation.

[1]) Compare also: CHANDLER, *Astr. Journ.* Vol. XIX, N°. 446 1898.

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Consequently, assuming the yearly motion to be constant, we find for the 14-monthly motion, both from the x and the y, values of the amplitude that decrease pretty regularly and pretty rapidly [1]). For the epoch we find from the first and the second period a fairly good agreement [2]), whereas from the third we find a decidedly deviating value.

The reality of this last deviation is not very probable, and this tends to diminish the force of the arguments which are in favour of the acceptation of a decrease of the amplitude, which might be explained by frictional influences [3]).

Physics. — "*The properties of the pressure curves for co-existing phases of mixtures*". By Prof. J. D. VAN DER WAALS.

In the "Verslagen en Mededeelingen der Akademie voor 1891" I have deduced an explicite expression for the pressure in the case that one of the phases of a mixture may be considered as a rarefied gas.

Since that time the course of the value of the pressure for different mixtures has been determined experimentally in different ways, so that we are enabled to test the given formula at the results of the experiments.

In the given formula an auxiliary quantity μ_x occurs, which represents: $pv - \int p\,dv$ or $pv - MRT\log(v-b_x) - \frac{a_x}{v}$, while the differential coefficient of this quantity with respect to x, viz. $\left(\frac{d\mu_x}{dx}\right)_{p\,T}$ may be approximately equated to $-\frac{d\frac{a_x}{b_x}}{dx}$.

As examples I draw attention to two shapes of these curves, which have been communicated in the Proceedings of this Academy: 1st. by Mr. HARTMAN for mixtures of CH_3Cl and CO_2 and 2nd by Mr. CUNAEUS for mixtures of Acetone and Ether. The curve traced by Mr. HARTMAN is remarkable on account of the simple shape of $p = f(x_1)$, which is almost a straight line, and that of Mr. CUNAEUS

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[1]) See also *Archiv. Néerl.* T. II, p. 475 (29).

[2]) See also *Archiv. Néerl.* T. II, p. 469 (23).

[3]) CHANDLER finds by his empirical theory that the amplitude varies periodically and decreases in the years considered. It seems to me however that the foundation of his formula is not yet sufficiently certain.

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on account of the fact, that in the curve $p = f(x_2)$ a distinct inflection point occurs.

The investigation in how far these curves agree with the given formula, will show that in one respect these two shapes may be considered as two limiting cases. For simplicity's sake I shall write henceforth μ_x instead of $\frac{\mu_x}{MRT}$. In the same way I shall represent $\frac{\left(\frac{d\mu_x}{dx}\right)_{pT}}{MRT}$ by μ'_x, and a similar expression for the second differential coefficient by μ''_x. The value of these quantities for $x = 0$ and $x = 1$ will be: μ_0, μ'_0, μ''_0 and μ_1, μ'_1 and μ''_1. Then p may be represented by the formula:

$$p = MRT(1-x_1)\, e^{\mu x_1 - x_1 \mu'_{x_1} - 1} + MRT\, x_1\, e^{\mu x_1 + (1-x_1)\mu'_{x_1} - 1}$$

or

$$p = p_0\ (1-x_1)\, e^{\mu x_1 - \mu_0 - x_1 \mu'_{x_1}} + p_1\ x_1\, e^{\mu x_1 - \mu_1 + (1-x_1)\mu'_{x_1}}$$

In general we cannot express p explicitely as function of x_2. But for the same value of p we have the following relation between x_1 and x_2 which may be derived from the equality of $\left(\frac{d\psi}{dx}\right)_{vT}$ for the two phases:

$$\frac{x_1}{1-x_1}\, e^{\mu'_{x_1}} = \frac{x_2}{1-x_2}.$$

If we take into consideration, that for very low temperatures, the value of μ'_x is approximately equal to $-\frac{d\frac{a_x}{b_x}}{dx}$, we may indicate a few limiting cases for the course of the quantities $\frac{a_x}{b_x}$, and the shapes which the pressure curves will assume in these limiting shapes. I have already assumed in my: "Théorie Moléculaire" that by approximation μ'_x may be equated to $-\frac{d\frac{a_x}{b_x}}{dx}$ and the deductions which have there been obtained from this assumption, have since been confirmed to such an extent by the properties of the plaitpoint curves for mixtures, which show a minimum critical temperature,

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that I feel justified in deriving further results from this approximation. I shall, however, first derive other equations which are independent of this approximation from the given values for p.

If we write $p = MRT e^{\mu' x_1 - x_1 \mu'_{x_1} - 1} \{1 - x_1 + x_1 e^{\mu'_{x_1}}\}$, then follows:

$$\frac{1}{p}\frac{dp}{dx_1} = -x_1 \mu''_{x_1} + \frac{(e^{\mu' x_1} - 1) + x_1 e^{\mu' x_1} \mu''_{x_1}}{1 - x_1 + x_1 e^{\mu' x_1}} =$$

$$= \frac{(e^{\mu' x_1} - 1)[1 + x_1 (1 - x_1) \mu''_{x_1}]}{1 - x_1 + x_1 e^{\mu' x_1}}.$$

This latter value agrees perfectly with that which is found by starting from the rigorously correct equation:

$$v_{21} \frac{dp}{dx_1} = (x_2 - x_1) \left(\frac{d^2\zeta}{dx_1^2}\right)_{pT},$$

if compared with v_2, the volume of a molecule in the vapour phasis, we neglect the value of v_1 and $\left(\frac{dv_1}{dx_1}\right)_{pT}$ and equate v_2 to $\frac{MRT}{p}$. We may namely put $\psi + pv$ for ζ; we find then:

$$\left(\frac{d\zeta}{dx_1}\right)_{pT} = MRT \log \frac{x_1}{1 - x_1} + \left(\frac{d\mu}{dx_1}\right)_{pT}$$

and

$$\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT} = \frac{MRT}{x_1 (1 - x_1)} + \left(\frac{d^2\mu}{dx_1^2}\right)_{pT}.$$

After elimination of x_2 we find:

$$\frac{1}{p}\frac{dp}{dx_1} = \frac{x_2 - x_1}{x_1 (1 - x_1)} \{1 + x_1 (1 - x_1) \mu''_{x_1}\} = \frac{(e^{\mu' x_1} - 1)[1 + x_1 (1 - x) \mu''_{x_1}]}{(1 - x_1) + x_1 e^{\mu' x_1}}$$

The following wellknown facts may be deduced from this equation: 1st. $\frac{dp}{dx_1} = 0$ if $e^{\mu' x_1} = 1$ or $\mu'_{x_1} = 0$ or $x_2 = x_1$ and 2nd $\frac{dp}{dx_1} = 0$ if $1 + x_1 (1 - x_1) \mu''_{x_1} = 0$ or $\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT} = 0$.

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From

$$\frac{dp}{dx_1} = p\,\frac{(e^{\mu'_{x_1}}-1)\,[1+x_1\,(1-x_1)\,\mu''_{x_1}]}{1-x_1+x_1\,e^{\mu'_{x_1}}}$$

we deduce

$$\frac{\frac{d^2p}{dx_1^2}}{\frac{dp}{dx_1}} = \frac{1}{p}\,\frac{dp}{dx_1} - \frac{(e^{\mu'_{x_1}}-1)+x_1\,e^{\mu'_{x_1}}\mu''_{x_1}}{1-x_1+x_1\,e^{\mu'_{x_1}}} + \frac{e^{\mu'_{x_1}}\,\mu''_{x_1}}{e^{\mu'_{x_1}}-1} + \\ + \frac{(1-2\,x_1)\,\mu''_{x_1}+x_1\,(1-x_1)\,\mu'''_{x_1}}{1+x_1\,(1-x_1)\,\mu''_{x_1}}$$

or

$$\frac{\frac{d^2p}{dx_1^2}}{\frac{dp}{dx_1}} = \mu''_{x_1}\left\{-x_1+\frac{e^{\mu'x_1}}{e^{\mu'x_1}-1}+\frac{(1-2\,x_1)}{1+x_1\,(1-x_1)\,\mu''_{x_1}}\right\} + \\ + \mu'''_{x_1}\,\frac{x_1\,(1-x_1)}{1+x_1\,(1-x_1)\,\mu''_{x_1}}.$$

Let us put some special cases:

Put

$$e^{\mu'x_1}=1 \text{ or } \mu'_{x_1}=0, \quad \ldots\ldots\ldots \quad (a)$$

then:

$$\frac{d^2p}{dx_1^2} = p\,\mu''_{x_1}\{1+x_1\,(1-x_1)\,\mu''_{x_1}\}$$

If μ''_{x_1} is positive, $\frac{d^2p}{dx_1^2}$ is also positive; so in this case there is a minimum pressure. But from the assumption that $MRT\mu'_{x_1}$ may be equated with $\frac{-\,d\left(\frac{a_{x_1}}{b_{x_1}}\right)}{dx_1}$ follows: $MRT\mu''_{x_1} = -\frac{d^2\left(\frac{a_{x_1}}{b_{x_1}}\right)}{dx_1^2}$. We conclude therefore, that at very low T there is a minimum pressure for that mixture, for which $\frac{a_x}{b_x}$ has a maximum value. A mixture with a maximum value for $\frac{a_x}{b_x}$ has, however, not been found as yet, and it is even doubted whether this will ever occur for normal substances.

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If μ''_{x_1} is negative, then $\frac{d^2p}{dx_1^2}$ is negative, when $1 + x_1(1-x_1)\mu''_{x_1}$ is positive. So there is for p a maximum value for that mixture which shows a minimum for $\frac{a_w}{b_w}$. And numerous instances of this have been found. If μ''_{x_1} has so great a negative value, that $1 + x_1(1-x_1)\mu''_{x_1}$ is also negative, then p has again a minimum value. That $1 + x_1(1-x_1)\mu''_{x_1}$ is negative, implies however, that $\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT}$ is negative, and can therefore only occur for unstable phases. And for this too we may say that it is very doubtful, whether this can ever be the case for mixtures of normal substances.

If

$$x_1 = 0, \quad \ldots\ldots\ldots \quad (b)$$

we find;

$$\left(\frac{d^2p}{dx_1^2}\right)_0 = p_1 \mu''_0 (2e^{\mu'_0} - 1)$$

If the pressure is increasing at $x_1 = 0$, then $\left(\frac{d^2p}{dx_1^2}\right)_0$ has the same sign as μ''_0. If the pressure should also increase on the side where $x_1=1$, and if there should therefore be a maximum pressure for a certain value of x_1, then the quantity $\frac{d^2p}{dx_1^2}$ has all over the curve $p = f(x_1)$ the sign μ'', which is necessarily negative. The supposition that we may put $MTR\,\mu''_{x_1} = -\frac{d^2\frac{a}{b}}{dx^2}$, makes the sign of μ''_x dependent on;

$$-2b_1^2b_2^2\frac{\frac{a_1}{b_1^2} + \frac{a_2}{b_2^2} - 2\frac{a_{12}}{b_1b_2}}{[b_1(1-x) + b_1x]^3},$$

at least if we may replace b_{12} by the approximate value $\frac{b_1+b_2}{2}$. But even though this should not be quite accurate, yet it is not to be expected that the value of μ''_x should deviate much from the given formula. The given formula makes the sign of μ''_x dependent

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on $\left(\frac{a_1}{b_1^2}+\frac{a_2}{b_2^2}-2\frac{a_{12}}{b_1 b_2}\right)$, so that all over the curve the sign remains invariable.

If on one of the sides the pressure should decrease, and if we put on that side $x_1 = 0$, then the value of $e^{\mu'_0}$ is smaller than 1. We get then $\frac{x_2}{x_1} < 1$. But not before $\frac{x_2}{x_1} < \frac{1}{2}$, the sign of $\left(\frac{d^2p}{dx_1^2}\right)_0$ will differ from that of μ''_0.

If we have the exceptional case that there is a maximum pressure just on one of the sides then $e^{\mu'_0} = 1$, and therefore $\left(\frac{d^2p}{dx_1^2}\right) = p_1 \mu''_0$. This is almost, if not quite the case for the mixtures of acetone and ether investigated by Mr. CUNAEUS. On the ether-side the pressure is maximum, and the simple shape of the curve $p = f(x_1)$, for which the curvature is always such that $\frac{d^2p}{dx_1^2} < 0$, follows immediately from this supposition.

In this curve of CUNAEUS we have the case that one of the mixtures has a minimum critical temperature, though it is one of the components, but on the other hand in the curve of HARTMAN we have almost, if not quite the case, that μ'_x is constant for all values of x, and that there is therefore no question of a minimum critical temperature — not even if we should take x far beyond the limits of $x = 0$ and $x = 1$. It is not to be expected that this will ever be rigorously the case. Only if we put for b_x the approximate value $b_1(1-x) + b_2 x$, $\frac{a_x}{b_x}$ would be a linear function of x, in case $\frac{a_1}{b_1^2}+\frac{a_2}{b_2^2}-2\frac{a_{12}}{b_1 b_2}$ is equal to zero. But even if we do not introduce this approximate value of b_x, we may at least imagine as limiting case such a value of $\frac{a_x}{b_x}$, that it differs little from a straight line between 0 and 1. As limiting case we may therefore put $\mu'_x =$ constant.

Then we get $\mu_{x_1} - x_1 \mu'_{x_1} = \mu_0$ and $\mu_{x_1} + (1-x)\mu'_{x_1} = \mu_1$, and

$$p = MRT(1-x_1)e^{\mu_0 - 1} + MRT x_1 e^{\mu_1 - 1}$$

or

$$p = p_0 (1-x_1) + p_1 x_1$$

Consequently $p = f(x_1)$ is exactly a straight line, which HARTMAN has found for mixtures of CO_2 and CH_3Cl by approximation.

Moreover, it follows immediately from the value which we have

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found for $\frac{d^2p}{dx_1^2}$, that if we always put μ''_{x_1} and so also μ'''_{x_1}, as equal to zero, the value of this quantity is always equal to zero, and the pressure must be represented by a straight line.

In this special case it is also possible to give $p = f(x_2)$ explicitely. We have namely as relation between x_1 and x_2:

$$\frac{x_2}{1-x_2} = \frac{x_1}{1-x_1} e^{\mu'-\mu_1} = \frac{x_1}{1-x_1} e^{\mu_1-\mu_0} = \frac{x_1}{1-x_1} \frac{p_1}{p_0}$$

or

$$1-x_1 = \frac{1-x_2}{1-x_2 + \frac{p_0}{p_1} x_2}$$

and

$$x_1 = \frac{\frac{p_0}{p_1} x_2}{1-x_2 + \frac{p_0}{p_1} x_2}$$

Substituting these values we find:

$$p = \frac{p_0 p_1}{p_1 (1-x_2) + p_0 x_2}.$$

The curve $p = f(x_2)$ traced by HARTMAN, resembles a hyperbola, but it deviates too much from it for the deviations to be ascribed to experimental errors. But in reality, these observations have been made at a too high temperature for considering the vapour phasis as a rarefied gasphasis. Specially for carbonic acid, where the pressure was even greater than 45 atmospheres, the deviations, caused by it, must have been considerable. It would be interesting to investigate whether at a lower temperature (HARTMAN observed at 9°,5) the vapourbranch would approach closer to a hyperbola.

We may in this case write for $p = f(x_2)$:

$$\frac{1}{p} = \frac{1-x_2}{p_0} + \frac{x_2}{p_1},$$

from which, as we are here concerned with gasphases, follows:

$$v = v_0 (1-x_2) + v_1 x_2.$$

If we take therefore an arbitrary quantity of the saturated vapour

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of the first substance, and also an arbitrary quantity of the saturated vapour of the second, and if they mix in a volume which is the sum of the two volumes, the mixture is again saturated vapour. This result deviates altogether from the law of DALTON applied to saturated vapour. But this law of DALTON will only hold good as an approximation, if the liquid, which would be formed through condensation, may be considered as unmixed liquid.

It is well-known that DANIEL BERTHELOT has put $a_{12}^2 = a_1 a_2$. I have refuted this opinion some time ago, first because the ground which was alleged for concluding to this relation, seemed incorrect to me, as it does still, but secondly because the great variety, which the critical phenomena of mixtures show, seemed to me to clash with the assumption of such a simple relation between a_{12}, a_1 and a_2. Since I have learned to ascribe many complications, which mixtures show, to the anomaly of the components themselves, a great many objections, which I had against the relation $a_{12} = \sqrt{a_1 a_2}$, have lost their weight, and any rate I think it desirable to keep in view at every phenomenon the possibility, that this relation should be fulfilled. If we do so also in this case, the condition that $\frac{a_x}{b_x}$ be a linear function of x_1, becomes at least by approximation the following:

$$\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 = 0$$

or the critical expressions of the components are the same. Now it is indeed remarkable, that in the mixture of HARTMAN, for which the critical temperatures are almost in the proportion of 3 to 4, the critical expressions differ comparatively little — that of CO_2 being equal to 73 and that of CH_3Cl to 65 or 66 atmospheres. The condition that the critical expressions must be the same for the components, is fulfilled if $T_{c_2} = T_{c_1} \frac{b_2}{b_1}$, so if the critical temperatures are proportional to the volumes of the molecules. And though this condition is not quite fulfilled for CO_2 and CH_3Cl, yet it is fulfilled in an incomparably greater degree than for the other examined mixtures, for which the substance with the smallest molecule possesses the highest critical temperature. So is in a mixture of acetone and ether the critical temperature of ether lower than that of acetone, whereas the volume of the molecules of ether exceeds that of acetone. For acetone and ether the condition $\frac{\sqrt{a_1}}{b_1} = \frac{\sqrt{a_2}}{b_2}$ is certainly not ful-

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filled and in close connection with this is the great difference in the curve determined by CUNAEUS as compared with that of HARTMAN [1]).

In what precedes we have been specially occupied with the difference in the course of $p = f(x_1)$ for these mixtures. Let us also pay attention to $p = f(x_2)$. As the elimination of x_1 from the equation:

$$\frac{x_1}{1-x_1}\, e^{\mu'_{x_1}} = \frac{x_2}{1-x_2}$$

is not possible, when μ'_{x_1} depends on x_1, p can generally not be expressed explicitely in x_2. Yet we may deduce formulae for $\frac{dp}{dx_2}$ and $\frac{d^2p}{dx_2^2}$, which are of importance for the determination of the different shapes of these curves.

From the two strictly accurate equations:

$$v_{21}\, dp = (x_2-x_1)\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT} dx_1$$

and

$$v_{12}\, dp = (x_1-x_2)\left(\frac{d^2\zeta}{dx_2^2}\right)_{pT} dx_2$$

follows, in case the second phasis is a rarefied vapour-phasis, and we may consequently put $v_{21} = v_2$ and $v_{12} = -v_2$:

$$\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT} dx_1 = \left(\frac{d^2\zeta}{dx_2^2}\right)_{pT} dx_2$$

or

$$\frac{dx_1}{x_1(1-x_1)}\left\{1 + x_1(1-x_1)\,\mu''_{x_1}\right\} = \frac{dx_2}{x_2(1-x_2)}.$$

When the second phasis follows the gas laws sufficiently, the second term is simplified to the form given here.

By means of this relation between dx_1 and dx_2 and of the relation $\frac{x_2}{1-x_2} = \frac{x_1}{1-x_1}\, e^{\mu'_{x_1}}$, we find:

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[1]) The value of a_{12} calculated by Mr. QUINT for mixtures of Cl H and $C_2 H_6$, however, does not fulfil the relation $a_{12} = \sqrt{a_1 a_2}$.

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$$\frac{1}{p}\frac{dp}{dx_2}=\frac{1}{p}\frac{dp}{dx_1}\frac{dx_1}{dx_2}=\left(1-e^{-\mu' x_1}\right)\left(1-x_1+x_1 e^{\mu' x_1}\right)$$

or

$$\frac{dp}{dx_2}=p\left(1-e^{-\mu' x_1}\right)\left(1-x_1+x_1 e^{\mu' x_1}\right)$$

It appears from this formula that p as function of x_2 presents a maximum or a minimum only when $e^{\mu x_1}=1$. In the case, that a longitudinal plait exists, there are two more values of x_1, for which p as function of x_1 might become maximum or minimum in the unstable region, but this is not the case for p as function of x_2. The curve $p=f(x_2)$ presents two cusps for the values of x_2, which are conjugated to those values of x_1, for which $1+x_1(1-x_1)\mu''_{x_1}$ should be zero. This I have already pointed out in the Théor. Mol.

In order to determine $\frac{d^2p}{dx_2^2}$ we differentiate the logarithm of the last equation, which yields:

$$\frac{\frac{d^2p}{dx_2^2}}{\frac{dp}{dx_2}}=\frac{dx_1}{dx_2}\left\{\frac{1}{p}\frac{dp}{dx_1}+\frac{(e^{\mu' x_1}-1)+x_1 e^{\mu' x_1}\mu''_x}{1-x_1+x_1 e^{\mu' x_1}}+\frac{e^{-\mu' x_1}\mu'_{x_1}}{1-e^{-\mu' x_1}}\right\}$$

or

$$\frac{d_2p}{dx_2^2}=\frac{dp}{dx_2}\frac{dx_1}{dx_2}\left\{\frac{2(e^{\mu' x_1}-1)}{1-x_1+x_1 e^{\mu' x_1}}+\mu'_{x_1}\left[\frac{2x_1 e^{\mu' x_1}}{1-x_1+x_1 e^{\mu' x_1}}-x_1+\frac{1}{e^{\mu' x_1}-1}\right]\right\}$$

Special cases are:

(*a*) Be $1+x_1(1-x_1)\mu''_{x_1}=0$, then $\frac{d^2p}{dx_2^2}=\infty$, as $\frac{dx_1}{dx_2}$ is ∞ in this case. We have already pointed out, that the curve $p=f(x_2)$ presents cusps in the points conjugated to these values of x_1.

(*b*) Be $\mu'_{x_1}=0$, then $\frac{d^2p}{dx_2^2}=p\,\frac{\mu''_{x_1}}{1+x_1(1-x_1)\mu''_{x_1}}$. If we compare this value with $\frac{d^2p}{dx_1^2}$, it appears, that at the point of contact the two curves $p=f(x_1)$ and $p=f(x_2)$ lie on the same side of the tangent. The curvatures however are unequal, except in the case, that for such a point $x_1=0$. For the mixture of acetone and ether

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this exception occurs at least approximately on the side of the ether.

(c) Be $x_1 = 0$, then $\left(\frac{d^2p}{dx_2^2}\right)_0 = p_0 \frac{2(e^{\mu'_0} - 1)^2 + \mu''_0}{(e^{\mu'_0})^2}$.

This equation shows, that $\left(\frac{d^2p}{dx_2^2}\right)_0$ will be negative only by exception; only when μ''_0 is negative and has a numeric value, greater than $(e^{\mu'_0} - 1)^2$. It may however occur, and that on both sides for mixtures with maximum-pressure. It the following three figures the curves $p = f(x_1)$ and $p = f(x_2)$, which may then occur, are drawn.

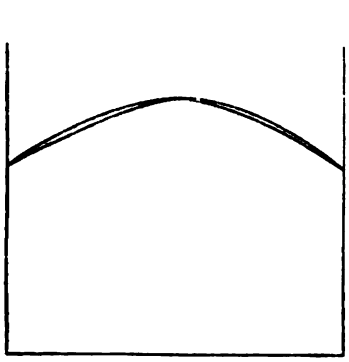

Fig. 1.

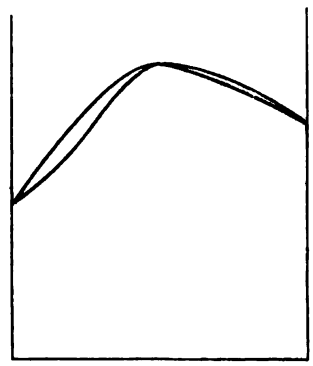

Fig. 2.

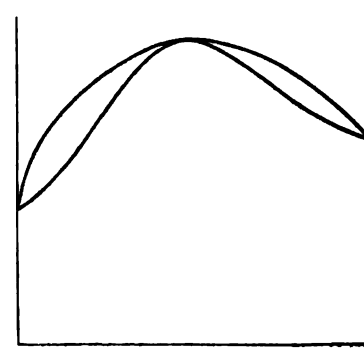

Fig. 3.

In fig. 1 a curve has been drawn, for which the maximum-pressure is not much greater than the pressures on both sides, and for which therefore $e^{\mu'_0} - 1$ has a small value, even on the sides. As in the case of a maximum-pressure the quantity μ'' is negative, $\left(\frac{d^2p}{dx_2^2}\right)_0$ may be negative on both sides.

In fig. 2 this is the case only on one side, while in fig. 3 the value of $(e^{\mu'_0} - 1)$ is supposed to be great enough, to cause $\frac{d^2p}{dx_2^2}$ to be positive on both sides.

The curve, traced by Mr. CUNAEUS relating to his investigation on acetone and ether is therefore to be considered as either the lefthand or the righthand half of fig. 3, and the point of inflection, which he has found, was to be expected, as on the side of acetone the value of $e^{\mu'_0} - 1 = \left(\frac{x_2 - x_1}{x_1}\right)_0$ is rather great, viz. 3,5.

From the value of x_1 and x_2, at which the point of inflection has been found, we may derive the value of μ''_{x_1} with the aid of the

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formula we have found for $\frac{d^2p}{dx_2^2}$. To that purpose we have to equate the factor of $\frac{dp}{dx_2}\frac{dx_1}{dx_2}$ to zero. If we substitute $\frac{x^2}{1-x_2}\frac{1-x_1}{x_1}$ for $e^{\mu' x_1}$, we may write this factor as follows:

$$\frac{1}{x_2-x_1}\left\{2\frac{(x_2-x_1)^2}{x_1(1-x_1)}+\mu''_{x_1}\left[2(x_2-x_1)^2+x_1(1-x_1)\right]\right\},$$

From this we deduce for the point of inflection:

$$-\mu'_{x_1}=\frac{2\frac{(x_2-x_1)^2}{x_1(1-x_1)}}{2(x_2-x_1)^2+x_1(1-x_1)}$$

In the experiments of Mr. CUNAEUS, we are not perfectly sure of the values of x_1 and x_2 for the point of inflection [1]). The numeric value of μ''_{x_1} cannot therefore be found with accuracy. Put $x_1=\frac{1}{2}$ and $x_2=\frac{2}{3}$, then the value of $-\mu''_{x_1}=\frac{8}{11}$, put $x_1=0{,}45$ and $x_2=0{,}65$, then the value of $-\mu''_{x_1}$, will be found slightly less than unity.

We can predict the course of the critical curves for mixtures of acetone and ether, from the properties of the pressure-curves for these mixtures at low temperatures. Let us imagine the critical curve, either the plaitpoint-curve or the curve of the critical points of contact of Cl H and C_2H_6, and let us take the upper half of it, i.e. that part, that lies above the minimum-temperature. That minimum temperature, the critical point of ether, will be the starting point. We have therefore reason to expect that mixtures of ether in which a little quantity of acetone has been solved, will present r. c. II. But for these critical curves also it is to be expected that they will deviate so slightly from one another, that it will be difficult to observe the retrograde condensation [2]).

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[1]) In the determination of the vapour-phasis by means of the refractive power, the circumstance, that the glass plates are covered with a condensed layer has an influence, which is probably large enough, to vitiate noticeably the values found for x_2.

[2]) Let us avail ourselves of this occasion to point out that the rule, given by Prof. KUENEN, to find *r c* II is not quite correct. Prof. KUENEN thought that *r c* II is to be looked for in mixtures of substances, of which that one, which has the highest critical temperature, has at equal temperatures also the highest vapour tensions. If we consider a plaitpoint curve, beginning exactly at the minimum critical temperature and therefore just beginning with *r c* II, the vapour tension of the component with the highest T_c will be lower than that of the other component; and the more so, when the difference between T_{c_2} and T_{c_1} is large.

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Let us write the value of $\frac{d^2p}{dx_2^2}$ also under the following form:

$$\frac{d^2p}{dx_2^2} = p\left[\frac{x_1(1-x_1)}{x_2(1-x_2)}\right]^2\left\{2\left[\frac{(x_2-x_1)}{x_1(1-x_1)}\right]^2 + \frac{\mu''_{x_1}}{1+x_1(1-x_1)\mu''_{x_1}}\right\}.$$

This form enables us to conclude to the curvature of the vapour-branch, if it has an unstable part [1]), in consequence of the presence of a longitudinal plait, which intersects the liquid branch. For this unstable part we have $1+x_1(1-x_1)\mu''_{x_1} < 0$, and μ''_{x_1} and $1+x_1(1-x_1)\mu'_{x_1}$ has the same sign. For this unstable part of the vapour branch we get therefore $\frac{d^2p}{dx_2^2} > 0$. Let us imagine two values of x_1, differing very little from that which makes $1+x_1(1-x_1)\mu''_{x_1}=0$, and chosen on either side of it, then $1+x_1(1-x_1)\mu''_{x_1}$ has either a very small positive value or a very small negative one, and therefore $\frac{\mu''_{x_1}}{1+x_1(1-x_1)\mu''_{x_1}}$ a very great positive or a very great negative value. This makes us conclude that the sign of $\frac{d^2p}{dx_2^2}$ changes for those values of x_2, which are conjugated to these, at which the liquid branch enters or leaves the unstable region. At the extremities of the unstable part of the vapour branch we find therefore cusps. Consequently the two stable parts of the vapour-branch end with a negative value of $\frac{d^2p}{dx_2^2}$. As a rule the vapour-branch at $x=0$ and $x=1$ has a positive value of $\frac{d^2p}{dx_2^2}$, therefore there are also as a rule two points, where $\frac{d^2p}{dx_2^2}$ will be equal to zero. Probably these points always lie near the cusps. The following figure gives a shape of the vapour branch fulfilling these conditions.

If before its end the vapour branch should possess a maximum, the second inflection point is unnecessary and its shape will be represented by fig. 5.

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[1]) We use here the term "unstable part" to indicate that the phases, represented by it, could only co-exist with unstable phases. Considered in themselves these phases are stable.

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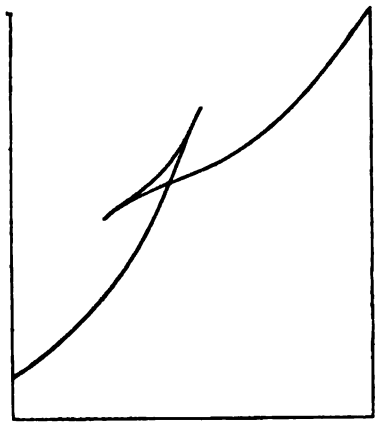

Fig. 4.

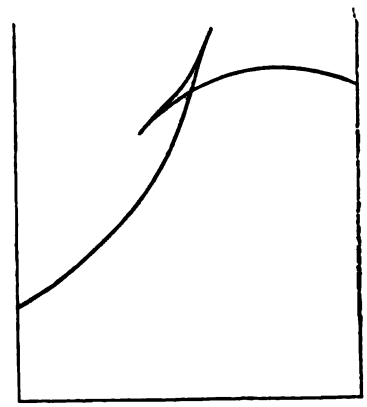

Fig. 5.

This latter figure represents the vapour branch of mixtures of phenol and water below the critical temperature of complete mixture.

If the second phasis is a rarefied gasphasis, the pressure of which is p, $p(1-x_2)$ represents the partial pressure of the first component and px_2 that of the second component. The value of these quantities is given by

$$p(1-x_2) = MRT(1-x_1)\, e^{\mu_{x_1} - x_1 \mu'_{x_1} - 1}$$

and

$$px_2 = MRT \quad x_1 \quad e^{\mu_{x_1} + (1-x_1)\mu'_{x_1} - 1}$$

and

$$p(1-x_1) = p_0(1-x_1) \quad e^{\mu_{x_1} - \mu_0 - x_1 \mu'_{x_1}}$$

and

$$px_2 \quad = p_1 x_1 \quad e^{\mu_{x_1} - \mu_1 + (1-x_1)\mu'_{x_1}}$$

We conclude from this:

$$\frac{dp(1-x_2)}{dx_1} = -p\frac{1-x_2}{1-x_2}\left\{1 + x_1(1-x_2)\mu''_{x_1}\right\}$$

$$\frac{dp\,x_2}{dx_1} = p\,\frac{x_2}{x_1}\left\{1 + x_1(1-x_1)\mu''_{x_1}\right\}$$

and

$$\frac{d^2p(1-x_2)}{dx_1^2} = p\frac{1-x_2}{1-x_1}\left\{x_1\mu''_{x_1}\left[1 + x_1(1-x_1\mu''_{x_1}\right] - \right.$$

$$\left. - \frac{d\left[1 + x_1(1-x_1)\mu''_{x_1}\right]}{dx_1}\right\}$$

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$$\frac{d^2px_2}{dx_{12}} = p\,\frac{x_2}{x_1}\left\{(1-x_1)\,\mu''_{x_1}\left[1+x_1(1-x_1)\,\mu''_{x_1}\right]+\right.$$

$$\left.+\frac{d\left[1+x_1(1-x_1)\,\mu''_{x_1}\right]}{dx_1}\right\}$$

By adding the two last conditions, we find:

$$\frac{1}{p}\,\frac{d^2p}{dx_1^2} = \mu''_{x_1}\left\{1+x_1(1-x_1)\,\mu''_{x_1}\right\}\left\{\frac{x_2(1-x_2)}{x_1(1-x_1)}+\frac{(x_2-x_1)^2}{x_1(1-x_1)}\right\}+$$

$$+\frac{x_2-x_1}{x_1(1-x_1)}\,\frac{d\left\{1+x_1(1-x_1)\,\mu''_{x_1}\right\}}{dx_1},$$

a form to which we may also reduce the form given before. From the value for the first differential coefficients we deduce, that for substances, which are perfectly miscible, the partial pressure of one component decreases, when the second component is substituted for a part of it. From this follows that the total pressure must be smaller than the sum of the tensions of the separate components. If $1+x_1(1-x_1)\,\mu_{x_1}$ should be negative, the partial pressure of a component increases on the other hand by substitution by the second component. Then it will be the question whether the partial pressure cannot rise so high, that it exceeds the initial value.

This question, however, cannot be solved without the knowledge of the properties of the function μ.

Physics. — Dr. E. VAN EVERDINGEN JR.: "*The* HALL*-effect and the increase of resistance of bismuth in the magnetic field at very low temperatures.*" II. (Communication N°. 58 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

1. From the measurements of the HALL-effect in bismuth at the boiling-point of liquid nitrous oxide and liquid oxygen, described in the Proceedings of 29 October 1899, p. 221 and 30 December 1899, p. 380, it appeared that the HALL-coefficient increased considerably with falling temperatures; it hence seemed desirable to determine this increase with greater accuracy. The measurements in liquid nitrous oxide had shown that the strength of the magnetic field had

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a considerable influence on the temperature-coefficient. Hence also the measurements in liquid oxygen ought to be taken with different strengths of the field. For the theory of the phenomenon it is necessary to know the resistance of the bismuth in the magnetic field at the same temperatures, in order to be able to calculate the angle through which the equipotential lines are turned. So I at first decided to measure, in say five different fields, HALL-effect, resistance and increase of resistance at the temperature of the room and at the boiling points of liquid nitrous oxide and oxygen. Afterwards a series of measurements at the boiling point of methyl chloride was added, and finally I completed the research by repeating the same measurements at the boiling point of water. As earlier researches [1]) have shown, that at still higher temperatures both HALL-effect and increase of resistance become very small, it might be considered superfluous to further raise the limit of temperatures.

Hence the temperatures range from — 182° C. te + 100° C. or from 91° to 373° on the absolute scale.

2. *Experimental arrangements.* In all the experiments except those at 100° C. the experimental plate of bismuth was mounted in the apparatus, described in § 6 of the communication of 30 December 1899 [2]). The only change made in this since then is that the strengthening-rim at the lower end of s_3 (see fig. 2 of that communication) has been omitted, and replaced by two glass tubes, fixed at both sides of the vessel b and over which the thin paper of s_3 is stretched.

In the modified section of the apparatus, fig. 1^a, these tubes are indicated by the letters i. This enabled me to adjust the vessel between the pole-pieces and to take it out again without altering the distance of the pole-pieces. In this manner 1st the apparatus remained quite closed at t_4, 2nd during the whole research the distance between the poles, and hence the strength of field for a given magnetising current, remained unaltered, and 3rd the repair of small faults in the various leads during the experiments was facilitated.

The apparatus continued to give satisfactory results and was at the end of the whole research still in good condition.

For the experiments at 100° C. the plate was placed in a copper

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[1]) See for instance LEBRET, Versl. der Verg. Kon. Ak. v. Wetensch. van 28 Sept. 1895, p. 103, Comm. Phys. Lab. Leiden N°. 19, p. 26; HENDERSON, Wied. Ann. 53, p. 912, 1894.

[2]) Versl. der Verg. van 30 December 1899, p. 380, Comm. N°. 53, p. 10.

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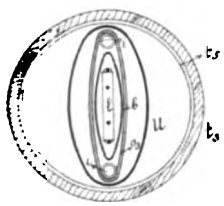

Fig. 1a.

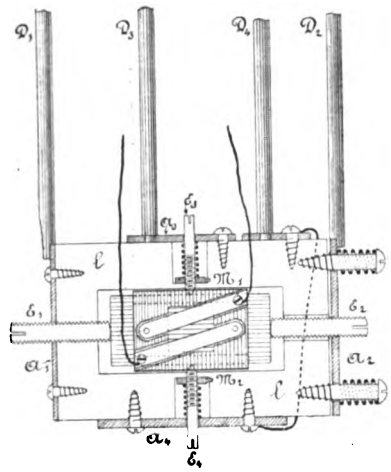

Fig. 1.

vessel, coated with asbestos and packed in wool, which was closed at the upper end by means of cork and through which steam was led.

Whilst therefore the baths of constant temperature presented no special difficulties, we had to bestow great care to secure good contact at the HALL- and resistance electrodes. In earlier experiments, soldering was deemed unsuitable, on account of the danger of spoiling the purity of the bismuth So here we had to use clamp-electrodes. It soon appeared that, for the contacts to resist the intense cooling, they ought to be made elastic. Steel springs could not be used, because of the disturbance they would have caused in the magnetic field; brass springs, which were tried first, appeared to lack sufficient elasticity, so that the contacts were nevertheless spoiled on cooling. These difficulties were overcome, for the most part at least, by using springs made of an alloy of Platinum with 30 pCt. of Iridium.

With reference to fig. 1 we will now describe how the plate of bismuth was fixed in the carrier in its final form.

For this purpose we first direct our attention to the perspective drawing on the right. There we see the plate of bismuth P stuck through the vertical slit of the frame R to which the Platinum-Iridium springs V_1 and V_2 are fixed by means of screws S_1 and S_2. To the extremities of these springs little Platinum pens are attached, which go through cylindrical holes in R and end on the horizontal line in the middle of the plate P. These constitute the resistance electrodes, and are about 10 mm. apart. The springs V_1 and V_2 are placed in slits of the frame in order not to increase the total

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breadth and are thus at the same time protected against damage. To make sure that the liquefied gases reach the plate the central portion of the vertical slit is widened and moreover large holes are made in the sides of the frame.

In the middle of the upper and lower planes there is a small hole O. Through this enter the secondary electrodes of the plate-carrier l, drawn in section in the figure. The primary-electrode E_1 has been screwed through the brass strip A_1 and through the frame l and is therefore not elastic. E_2 on the contrary has been screwed only through the brass plate A_2 and goes freely through l, whilst A_2 is elastically attached to l. The secondary electrodes E_3 and E_4 are also elastically attached; they go freely through the brass plates A_3 and A_4, but are screwed through the nuts M_1 and M_2, which are pressed inwards by spirals of Platinum-Iridium, whilst a pin prevents them from turning together with the screws. The plate A_1 is connected by a thin insulated wire to the copper wire D_4. To the wires $D_1 \ldots D_4$ the thin copper wires m_1, m_2, n_1, n_2 (see fig. 1 Comm. N°. 53) are fixed by means of screw-connexions. From the screws S_1 and S_2 copper wires of 0,1 mm. diameter go out of the apparatus through the same glass tubes as m_1 and m_2 for the measurement of the resistance.

In the experiments at 100° C. the plate-carrier l was made of wood and the frame R of ivory; in the other experiments both were made of ebonite.

3. *Measurements of the* HALL-*effect.* The plate of bismuth which served in all experiments was not the same as that used in the preliminary experiments of Communication N°. 53, as the latter was broken, when further observations had already been made at some temperatures. The new plate was however obtained in the same manner by electrolysis; the current for this was chosen somewhat smaller than on the former occasion. The resistivity of this plate appeared to be a little smaller than that of the other, while the HALL-effect and the increase of resistance were somewhat larger; this indicates that this bismuth is a little purer. That however complete purity is not yet attained follows from the most sensitive criterion: the resistance out of the magnetic field at low temperatures, to which we will draw attention once more further on.

The dimensions of the plate were: length 21 mm., breadth 9,1 mm., thickness 0,795 mm.

Of the method of observation nothing new need be mentioned [1]).

[1]) Verslag d. Vergadering van 30 Mei 1896, p. 47. Comm. N° 26, p. 8.

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As with the last measurements of Comm. N°. 53 the resistance in the secondary circuit was measured for both directions of the magnetic field immediately after the determination of the resistance required in the compensative-circuit. In order to be able to quickly perform this measurement I proceeded in the following way: As a commencement I observed the deflection of the galvanometer caused in the secondary circuit by a WESTON-element when a resistance of 50.000 Ohms was inserted and the poles of the element were connected to two of the mercury-cups of the commutator of this circuit [1]), the other two mercury-cups being connected by a short copper wire. As this deflection remained constant during a series of observations, it need be observed only once. For the measurement of the resistance the deflection was observed again after a shunt had been made between the two first mentioned mercury-cups with a known resistance about equal to that of the secondary circuit, so that the deflection was reduced to about one half of its former value. If we call a the total deflection, b the reduced deflection and w the resistance of the shunt, then the resistance of the secondary circuit is $w\frac{a-b}{b}$.

First we give the results for the HALL-coefficient R in various magnetic fields M (in C. G. S. units).

HALL-coefficient R.

Temperature in degrees Centigrade.

+ 100°		+ 11° 5		— 23°		— 90°		— 182°	
M	R	M	R	M	R	M	R	M	R
1090	7.23	1050	13.24	1060	16.90	1020	27.88	1050	61.8
2200	7.16	2100	12.69	2120	15.83	2140	24.80*	2100	54.5
3920	6.99	3100	12.06	3110	14.98	3070	22.87	3830	46.2*
4800	6.87	4440	11.42	3770	14.55	3730	21.85	6050	39.8
4870	6.82	6010	10.61	4320	14.13	4370	21.10		
5970	6.75			4440	13.94	5180	19.97		
				5260	13.39	6050	18.68*		
				6010	12.90				

[1]) See my thesis, plate III.

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These results are represented graphically in fig. 2, where the little crosses indicate observed points.

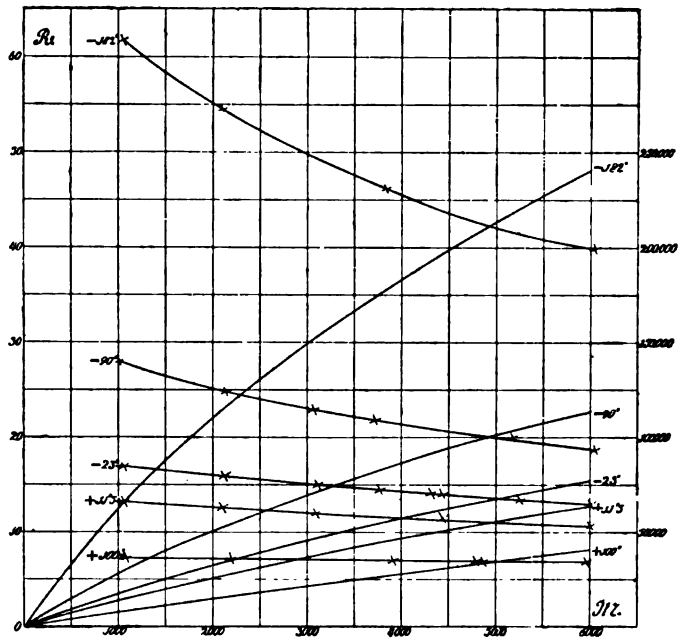

Fig. 2.

When a series of observations was finished usually one or more of the determinations were repeated; on the one hand this gave a means of testing the accuracy of the measurements, on the other hand of testing the constancy of the temperatures. With + 100° C. the two measurements in a field of about 4800 may serve for a test; with — 23° C. those in a field of about 4400; with the temperatures — 90° and — 182° an asterisk in the table indicates that the measurement was repeated *and gave the same result*; the value 46.2 in the field 3830 at — 182° C. is the result of *three* measurements in complete agreement [1]).

Usually before or after a series of measurements a determination at ordinary temperature was made; these too agreed always well, so that, at least during the three months occupied by the research, no traces of a variation with time are to be detected.

With the experiments in methylchloride and nitrous-oxide no trouble was experienced in keeping the vessel filled with liquid for about 5 hours, so that there was abundant time for observations.

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[1]) The results, obtained with the plate afterwards broken, usually also agree with those above mentioned.

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With the experiments in liquid oxygen however the vessel was usually nearly empty before a new quantity of liquid could be admitted, hence in this case the number of measurements was somewhat reduced.

During the experiments at 11°,5 C. air was sucked through the apparatus in order to ensure equilibrium of temperature with the surroundings.

The results wholly confirm the rule formulated before[1]: that the variation of the HALL-coefficient with the magnetic field is larger the lower the temperature, or: that the influence of temperature on the HALL-coefficient is largest in weak fields.

The value **61,8** of the HALL-coefficient in the weakest field at — 182° C., is again considerably larger than the highest value obtained before[2] (in the magnetic field 4400).

By means of the curves drawn through or between the observed points the HALL-coefficients in the fields 1000, 2000 . . . 6000 were interpolated, and multiplied by the corresponding magnetic fields. The values of the thus obtained product RM, which may be considered as a measure of the total transverse difference of potential, are represented in the same figure. The scale value of these ordinates is indicated on the right hand side.

Finally in fig. 3 the variation with temperature of the HALL-

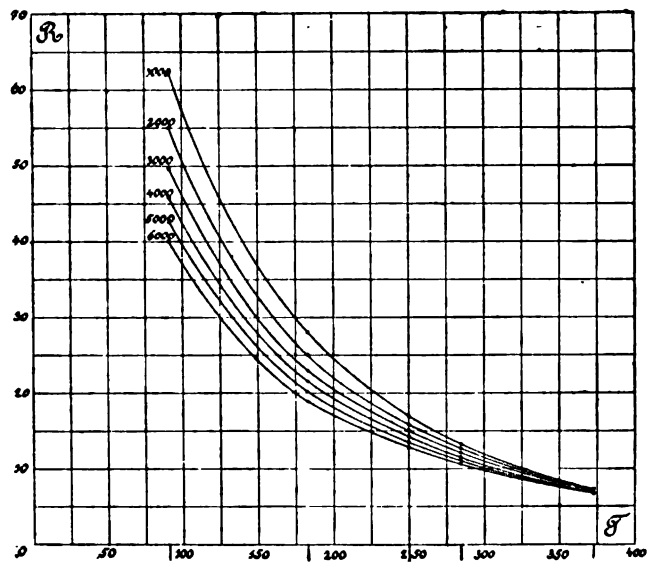

Fig. 3.

coefficient for given values of the field was represented for the fields

[1]) Versl. 30 Mei '96, p. 59. Comm. N° 26, p. 20.
[2]) " 30 Dec. '99, p. 382. Comm. N° 53, p. 13.

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1000 to 6000. The data for this figure are also given in the table below.

HALL-coefficient R.

$T_{abs.}$	Magnetic field in C. G. S. units.					
	1000	2000	3000	4000	5000	6000
91	62.2	55.0	49.7	45.8	42.6	40.1
183	28.0	25.0	22.9	21.5	20.2	18.9
250	17.0	16.0	15.1	14.3	13.6	12.9
284[5]	13.3	12.7	12.1	11.5[5]	11.0[5]	10.6
373	7.28	7.17	7.06	6.95	6.84	6.72

It appears that in all fields the increase of the HALL-coefficient with falling temperature is approximately proportional to T^{-a}, where a is greater than unity.

4. *Measurements of resistivity and increase of resistivity.* For the method of observation reference may be made to Comm. N°. 48 [1]). (The resistance in the circuit containing the resistance-electrodes was measured in the same manner as that of the secondary circuit for the HALL effect).

In the experiments before a determination of the resistance of the bismuth in the magnetic field a determination without magnetic field was always made, and the increase of resistance caused by the magnetic field was calculated by a direct comparison of these resistances.

Hence we obtained for the resistance out of the magnetic field as many values as there were measurements. The agreement between these values was always very satisfactory, once more confirming that the temperature remained constant during the experiments. For, these observations were made at the same time with those for the HALL-effect.

For the calculation of the resistivity we further want the dimensions of the plate in the transverse section, which were known accurately, and the distance of the resistance-electrodes, which could not be obtained with the same accuracy, were it only because the planes of contact were rather large as compared with their distance. In

1) Versl. 25 Maart '99, p. 486. Comm. N°. 48, p. 6.

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order to get nevertheless at the various temperatures a good correspondance in the values of the resistivity, immediately before or after a series of measurements a determination of the resistance of the bismuth at ordinary temperature was made. In this manner we got an accurate determination of the ratio between this resistance and that at the lower or higher temperature. Finally for the resistivity at 11°.5 C. a value was accepted as right and from this the values at other temperatures were calculated. The difference between the value calculated in this manner and that obtained directly was in the most unfavourable case only 2 pCt.

A correction for contraction of the plate of bismuth and the plate-carrier by cooling would be too small to be worth considering.

We first communicate the results for the percentage increase of the resistivity in the magnetic field.

Percentage increase of resistivity Δr.

Temperature in degrees Centigrade.

+ 100°		+ 11°5		— 23°		— 90°		— 182°	
M	Δr	M	Δr	M	Δr	M	Δr	M	Δr
2200	0.9	1050	0.9	1060	1.5	1020	3.5	2050	35.9
3950	2.6	2060	3.0	2140	5.2	2140	12.5	3730	90.2
4830	4.0	3060	5.8	3110	9.7	3100	23.4	4740	127.1
6100	5.8	4450	10.4	3790	13.2	3760	29.9	6000	175.7
		6030	16.6	4410	16.6	4150	34.6		
				5250	21.5	5200	47.7		
				6050	26.5	6110	59.6		

It appeared that the formula for the increase of resistance given in Comm. n°. 48

$$\Delta r = \frac{C_2 M^2}{1 + C_1 \sqrt{M^2}}$$ [1])

represents very satisfactorily the determinations at all the temperatures of observation. For brevity I shall not mention here the calculated

[1]) Versl. 25 Maart '99, p. 485. Comm. N°. 48, p. 4.

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values and communicate only the values of C_1 and C_2, and the largest deviations between calculation and observation.

$T_{abs.}$	C_1	C_2	Largest deviation.
91	0.312	14.027	3.7
183	0.285	4.381	0.69
250	0.219	1.681	0.34
284°	0.187	0.968	0.29
373	0.069	0.220	0.12

In fig. 4 the curves are drawn through the calculated points, the crosses indicating the observations. They also show a good agreement, while the deviations are not systematically distributed.

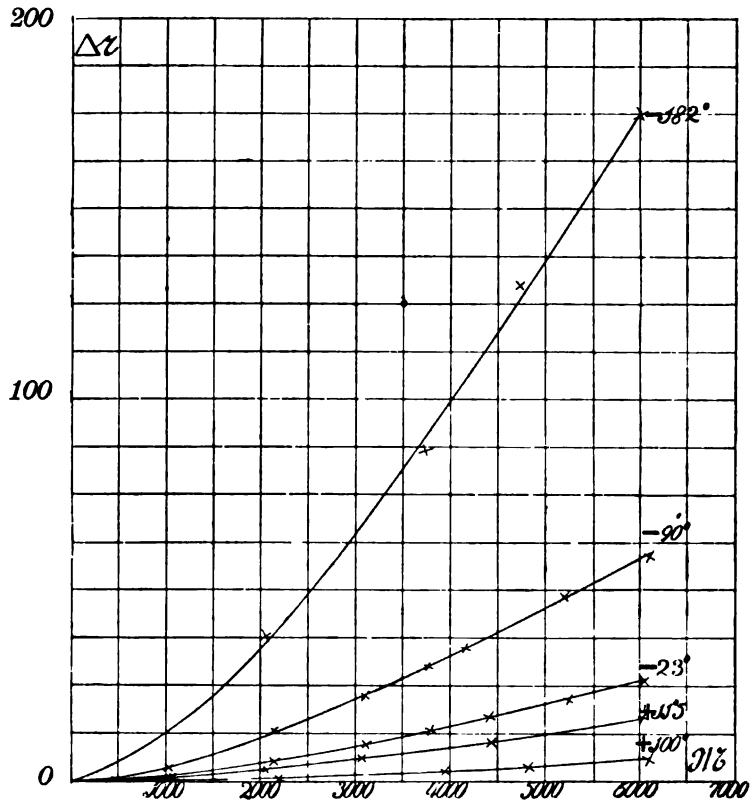

Fig. 4.

By means of the values of the percentage increase calculated from this formula and the results for the resistivity out of the magnetic

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field (second column) the following values for the resistivity in the magnetic field have been found.

Resistivity r (multiplied by 10^{-5}).

$T_{abs.}$	Magnetic field in C. G. S. units.						
	0	1000	2000	3000	4000	5000	6000
91	1.711	1.894	2.316	2.826	3.418	4.054	4.718
183	1.526	1.578	1.701	1.853	2.023	2.219	2.423
250	1.600	1.623	1.683	1.744	1.828	1.920	2.020
284[5]	1.690	1.703	1.738	1.783	1.839	1.904	1.967
373	2.094	2.098	2.111	2.129	2.152	2.180	2.212

These results are represented graphically in fig. 5.
If we compare them with those of FLEMING and DEWAR [1]), it

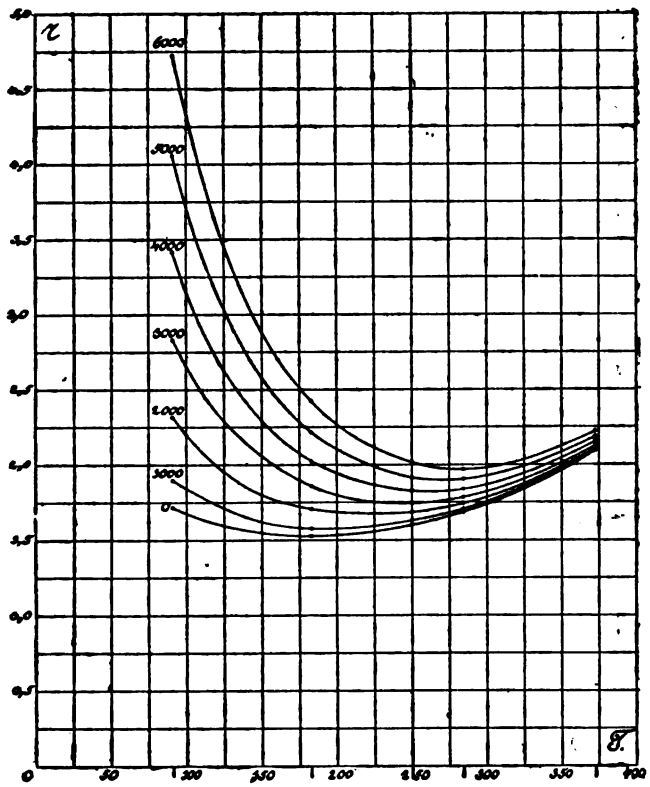

Fig. 5.

[1]) Proc. Roy. Soc. 60, p. 425, 1896.

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appears that the general character of the curves is the same. The resistivity out of the magnetic field however does not continuously decrease here, as with the electrolytic bismuth from HARTMANN and BRAUN, but reaches a minimum and then rises again to about the value it showed at ordinary temperature. FLEMING and DEWAR [1]) found a similar behaviour with some samples of bismuth carefully prepared by chemical means; my curve happens to coincide practically with the one they found with „MATTHEY's Bismuth (*B*)". Hence very likely the bismuth of my plate also contains only a very slight impurity; for the present research this impurity is of no consequence.

5. *Angle of rotation of the equipotential lines.* A combination of the results of § 3 and 4 enables us to calculate the angle, through which the equipotential lines are turned in the magnetic field. Thus if the product RM is devided by the resistivity r, the quotient is equal to the tangent of that angle. Again the quotient of R and r is equal to that same tangent for a magnetic field 1, a quantity first introduced by LEDUC [2]) and which we shall call D as he did. From what follows it will appear that this quantity has a simpler theoretical meaning than the HALL-coefficient R.

The results of the calculation of D are found in the following table and in fig. 6.

Rotational coefficient D (multiplied by 10^5).

$T_{abs.}$	Magnetic field in C. G. S. units.					
	1000	2000	3000	4000	5000	6000
91	32.9	23.8	17.6	13.4	10.5	8.5
183	17.7[5]	14.7	12.3[5]	10.6	9.1	7.8
250	10.48	10.48	9.50	8.66	7.82	6.39
284[5]	7.81	7.31	6.79	6.28	5.80	5.39
373	3.47	3.40	3.32	3.23	3.14	3.04

In order to facilitate a survey of the influence of temperature

1) Proc. Roy. Inst. June 5, 1896, p. 16.

2) La Lumière Electrique 29, p. 230, 1888.

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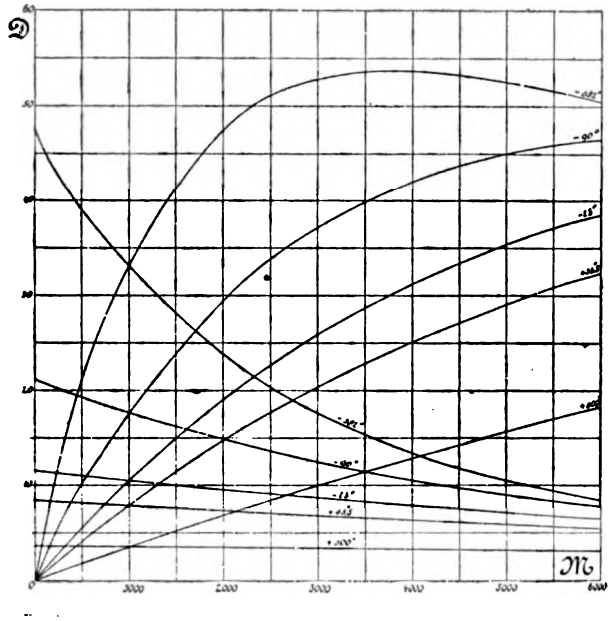

Fig. 6.

and of magnetic field on D, I tried to represent the results for each of the five temperatures by a formula of the same form, and succeeded very well with the formula

$$D = \frac{D_0}{1 + D_1 \sqrt{M^2} + D_2 M^2}.$$

As in the case with the increase of resistance I shall give here only the constants, and the largest deviations from the calculated values. M was expressed here in the unit 1000 C.G.S., D in the unit 10^{-5} C.G.S.

$T_{abs.}$	D_0	D_1	D_2	Largest deviation.	$\frac{D_0}{D_1}$
91	47.48	0.3708	0.06603	0.14	128
183	21.13	0.1850	0.01714	0.18	114
250	11.50	0.0885	0.00736	0.03	130
284[5]	8.40	0.0663	0.00451	0.03	126
373	3.53	0.0155	0.00188	0.002	(227)

Fig. 7 contains the curves drawn to represent these formulae.

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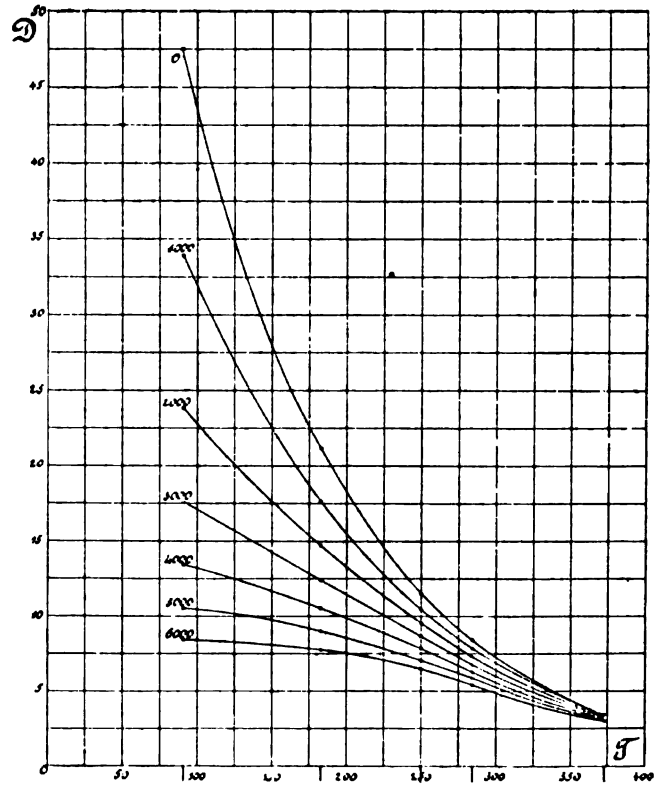

Fig. 7.

D_0 is evidently the limit to which D approaches in very weak fields; this quantity is best adapted to form a judgment of the influence of temperature alone, as the influence of the magnetic field on the resistivity of bismuth may be neglected in such weak fields.

The coefficients D_0 and D_1 show a somewhat parallel course, as appears from the column headed $\frac{D_0}{D_1}$. Only the ratio at $T = 373°$ differs considerably; but here the line is almost straight and the whole variation with M small, so that the interpolation and with this the deduction of the coefficients becomes a little arbitrary. If we put $D_2 = 0$ for $T = 373°$, then the results for that temperature are represented to within differences of at most 0,03 by a formula with $D_0 = 3{,}56$ and $D_1 = 0{,}0266$, and hence with $\frac{D_0}{D_1} = 134$.

All coefficients are approximately proportional to T^{-a}, where a is greater than 1, especially for D_2.

Whilst, as we saw before, even at the lowest temperature the product RM increases throughout with M, we see here in fig. 6 that

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the product DM (drawn on a scale 1000 times smaller than D) shows a maximum at $-182°$ C. [1]). This peculiarity also is borne out by the formula, in which above a definite value of M the term D_2M^2 dominates; one might even deduce from it that in strong magnetic fields (17.000 to 20.000) the product would have its highest value at the *highest* temperature, which does not seem very probable. But it is possible that with the very high values which the transverse difference of potential reaches in this plate a disturbance is caused by the electrodes for the primary current, which are 3,5 mM. thick and hence can certainly not be considered as mere points, so that we do not measure the full HALL-effect. VON ETTINGSHAUSEN and NERNST [2]) found that the full HALL-effect was almost reached when the ratio of breadth to length was as 2 to 3, and the primary electrodes fully covered the sides. In their research however they did not obtain nearly such high values of R. If therefore my presumption is justified, one might suppose that the true effect is represented by the same formula with $D_2 = 0$. DM approaches then for all temperatures to a *common* limit $\frac{D_0}{D_1}$.

6. *Remarks on the theory of the phenomenon.*

These results may contribute to the determination of the temperature-functions $\nu\Theta'$ and Θ_1 in VOIGT's thermo-dynamical theory [3]).

The theory of the HALL-phenomenon, based upon the recent theories of the conduction of electricity in metals, such as that of LORENTZ [4]) or as a part of the "Electron-theory of metals", after DRUDE [5]), is at this moment still in the nascent state. Yet I think it possible even now to draw from the foregoing some conclusions with respect to that theory and to indicate how far this theory is able to give an explanation of the influence of temperature and of magnetic field on the constants which represent the HALL-effect.

As yet the only completely elaborated theory on this basis is that of RIECKE [6]). This gives the following formula [7]) for the HALL-coefficient:

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[1]) This maximum 0,536 is smaller than the value 0,740, given in Communication N°. 53. There however a preliminary value for the resistance was assumed which now appears to have been too low.

[2]) Wien. Sitz. Ber. 94, p. 568, 1887.

[3]) Wied. Ann. 67, p. 717, 1899.

[4]) Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern. Leiden, 1895.

[5]) Ann. der Physik. 1, p. 566, 1900.

[6]) Wied. Ann. 66, p. 345 en 545, 1898.

[7]) ib. p. 563.

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$$P = \frac{1}{\gamma} \frac{u^2 g_n - v^2 g_p}{u g_n + v g_p}$$

(γ = conductivity, u and v velocities of the charged particles caused by a potential gradient 1, g_p and g_n velocities caused by a temperature gradient 1).

Hence for D we find:

$$D = \frac{u^2 g_n - v^2 g_p}{u g_n + v g_p}.$$

According to RIECKE's theory u and v, and likewise g_p and g_n, are to be multiplied by the same factor for variations of temperature. From this it follows immediately that with change of temperature D is multiplied by the same factor as u or v.

Precisely the same result is deduced from the formula for the HALL-phenomenon in electrolytes, given in my thesis for the doctorate and in Comm. N°. 41 [1]), which wholly agrees with a formula deduced by WIND [2]) for the HALL-effect in metals. This reads:

$$R = r\,(u - v) \quad \text{hence} \quad D = (u - v).$$

If u and v undergo proportional variations with temperature D here also is multiplied with the same factor. The same would apply if u were many times greater than v, or the reverse. Therefore we shall assume for simplicity that the temperature-variation of D is controlled by that of u. According to the deductions in my thesis and to the theories of RIECKE and DRUDE

$$u = K \frac{l}{\mathrm{v}} \text{ [1])}$$

where K is independent of the temperature, l is the mean free path and v the mean velocity of the charged particles.

The suppositions made regarding the variations of l and v with temperature will hence determine the temperature factor of u.

RIECKE assumes:

$$l = l_0 (1 - \beta t)$$

$$\mathrm{v} = c \sqrt{T} (1 + \delta t)$$

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[1]) Thesis p. 107. In Comm. n°. 41 (Versl. d. Verg. 28 Mei 1898, p. 53, Comm. n°. 41 p. 9.) the formula for D contains another numerical factor.

[2]) Verh. Kon. Ak. v. Wet. Deel V N°. 3, § 17.

[3]) Thesis p. 104, RIECKE l. c. p. 277, DRUDE l. c. p. 575.

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hence the temperature factor of D becomes

$$\frac{1-(\beta+\delta)t}{\sqrt{T}}$$

where t means the temperature in centigrade degrees, and T the absolute temperature. The shape of this formula remains the same even if we should assume that v is strictly proportional to $\sqrt{T}$, as then only δ becomes zero.

If this formula is applied to the values of D_0, these appear to be reconcilable with it if $(\beta+\delta)$ (or β in the limit) is *positive*. In the latter case this means that the mean free path decreases with rising temperatures, which is according to RIECKE's assumptions.

When the range of temperature from 373 to 91 (abs.) is subdivided into three parts, we find as mean values for $(\beta+\delta)$ or β

$373 - 284^5$	0,00549
$284^5 - 183$	0,00898
$183 - 91$	0,01481

RIECKE himself calculates [1]) β and δ from the variation of the conductivities for heat and electricity in bismuth between 0° en 100° C., however using a relation between δ and another temperature-coefficient which is perhaps not unobjectionable; he finds β to be 0,00205, δ — 0,0000103, hence

$$\beta+\delta = 0{,}00204$$

a result of the same order of magnitude. Also considered apart the results deduced above need not be called improbable.

Calculating however the values for the same temperature coefficient in the magnetic field 6000, we find

$373 - 284^5$	0,00382
$284^5 - 183$	0,00159
$183 - 91$	—0,00207

It seems impossible that the value of β could be so different in the magnetic field.

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[1]) l.c. p. 573.

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An explanation of this apparent contradiction can be obtained by means of the hypothesis, that in the magnetic field the number of free charged particles is diminished, the same hypothesis, which leads to an explanation of the increase of the resistance in the magnetic field, and of the proportionality between longitudinal-effect and increase of resistance [1]).

Indeed in my thesis I ventured the supposition [2]), that this decrease is caused in the following way, that the particles with velocities smaller than a certain amount (say smaller than a critical velocity x) are caused to move in closed orbits in the magnetic field and cease to partake in the transference of the current. It is evident that the mean velocity of the remaining, free particles will be greater than the mean velocity of *all* particles. Hence in our formula we ought to insert for v the mean velocity of all particles, *multiplied by a factor q*. In a magnetic field of definite strength the critical velocity x has a definite value which in my thesis I assumed proportional to M. The lower the temperature, the larger the number of particles with velocities below the critical. If now for a moment we assume MAXWELL's law for the distribution of the velocities of the free particles, then it appears that the rate of increase of q is greater, the larger the ratio of the critical velocity to the mean velocity of all particles, or, that the rate of increase of q itself increases with falling temperatures.

For a constant value of the magnetic field and hence of x, this result may be introduced easily into the formula by giving to δ a rather large negative value for a magnetic field of 6000; in this manner the negative sign of $(\beta + \delta)$ would be explained.

We have not yet the data to enquire whether our hypothesis gives a quantitative explanation of the phenomena. But we may notice that the hypothesis is sufficient to also explain other particularities in the variation of the quantity D, as may be seen by reference to fig. 6 and 7.

The decrease of D with increasing magnetic forces at constant temperature (fig. 6) is explained immediately by the increase of x; for the mean velocity of all particles remains constant, and q consequently increases. This decrease of D is most rapid at the lowest temperature; this also is explainable, as then the critical velocity

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[1]) See Versl. Kon. Akad. v. Wetensch. 25 Maart 1899, p. 496. Comm. N°. 48 p. 23.
[2]) See p. 112.

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is greatest as compared with the mean velocity and the rate of increase of q is larger. If the critical velocity happened to become much larger than the mean velocity, v would become approximately independent of temperature; hence this might be the explanation of the small influence of the temperature in strong fields, and render it probable that in a very strong field D would become independent of the temperature. A maximum of the quantity DM at — 182° C. would not be explained, but one might expect an approach to a constant value, as the critical velocity and hence the mean value of v for the free particles increases proportionately to M, so that D would decrease nearly proportionately to the inverse of M, which is completely in agreement with our formula, if we put in it $D_2 = 0$.

Our hypothesis throws also some light upon the reason why the increase of the resistance in the magnetic field for small strengths is proportional to a power of M higher than first. For if we assume MAXWELL's law, then the probability that a particle has a velocity smaller than x is proportional to $\int_0^x x^2 e^{-x^2}\,dx$; for very small values of x we may take e^{-x^2} equal to unity, and find then that the number of particles with velocities smaller than x would be proportional to the third power of x, which means to the third power of M. The large increase of the resistance at low temperatures can be explained by the decrease of the mean velocity as compared with the critical velocity. Finally we remark, that, as at — 182° C. the resistance is increased nearly in the ratio of 1 to 3 in a magnetic field of 6000, it hence seems that about $^2/_3$ of the free particles lose their freedom in that case. At 100° C. on the contrary this number is very small, so that between these temperatures q should undergo a considerable change. This is in agreement with the large variation of the value of $(\beta + \delta)$.

This survey is of course only superficial and leaves several questions undiscussed. I think however that it affords sufficient reason to assume, that with the introduction of this hypothesis in the electron-theory of metals a step has been made in the right direction.

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Chemistry: — "*On the system:* [Bi_2O_3—N_2O_5—H_2O]". By Prof. J. M. VAN BEMMELEN.

Dr. G. M. RUTTEN has occupied himself in the Inorganic chemical Laboratory of the University of Leiden with the investigation of the system

$$[Bi_2O_3 - N_2O_5 - H_2O]$$

according to the phase rule. He also has, when studying the solid phases, subjected the observations of former investigators (HEINTZ, GLADSTONE, BECKER, JANSSEN, RUGE, YVON, LÜDDECKE, DITTE and others) on the basic nitrates and the so-called "Magisterium Bismuthi" to a critical investigation.

His results were as follows:

A. *The solid phases.*

1. *The neutral salt* $Bi_2O_3.3N_2O_5.10H_2O$ (in future called briefly Z_{10} [1])). This formula accepted of late years has been found correct. The salt does not possess a true melting point as formerly stated (72°), but it decomposes at 75°,5 into a liquid and the basic salt $Bi_2O_3.N_2O_5.H_2O$ (B_{1-1-1}).

The prismatic, triclinic crystals exhibit an angle of extinction of 26°.

Two further hydrates of the neutral salt were discovered: Z_4 and Z_3.

II. *The neutral salt* Z_3 (with 3 Mols. of H_2O). It was obtained at the ordinary temperature from Z_{10}, or from Bi_2O_3 by addition of anhydrous nitric acid, in regular crystals as beautifully formed rhombic dodecahedrons. It should be mentioned that its composition could not be determined directly, because it was not possible to separate the crystals completely from the syrupy mother liquor. The composition was deduced by means of SCHREINEMAKERS' method of calculating, from the graphical construction in an equilateral triangle of the compositions: 1st of two different mother liquors which were in equilibrium with crystals of Z_3, and 2nd of the crystals themselves with some of the mother liquor still adhering. The same applies to the salts presently to be described Z_4 and B_{1-2-1}, which also could not be separated from the adhering mother liquor.

III. *The neutral salt* Z_4 (with 4 mols. of H_2O). A definite mode

[1]) In future the salts which contain 1 mol. of Bi_2O_3, 3 Mol. N_2O_5 and 10 or 4 or 3 Mol. H_2O will be briefly called Z_{10}, Z_4, Z_3; similarly the basic salts will be written $B_{n_1-n_2-n_3}$ if they contain n_1 Mol. of Bi_2O_3, n_2 Mol. N_2O_5 and n_3 Mol. H_2O

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of preparing this cannot yet be given. The salt was accidentally discovered when making efforts to realize points of a quadruple line in the system [Z_{10}, Z_3, L, G] [1]). The crystals differ from Z_3 and Z_{10} as they are not regular and have an angle of extinction of 90°.

IV. *Hydrate of Z in a colloidal state.* This was discovered when anhydrous nitric acid was dropped into a mixture of Z_{10} with a strong solution of Bismuth nitrate. A salt was deposited in the form of transparent jelly which enclosed all the mother liquor. The colloidal state lasted, however, but a short time. Very soon small crystals were deposited which made the impression of octahedrons, perhaps Z_3 or another hydrate. They have not yet been investigated.

V. *The basic salt* B_{1-2-2}. In one experiment Z_{10} was decomposed at 75° (which gave rise to the formation of B_{1-1-1}), then mixed with Z_3, heated to 80° and cooled down to 68°. A crystalline salt was produced which differed in form from Z_{10} and Z_3, had an angle of extinction of 40°, and the composition B_{1-2-2}. More analyses are however desirable.

VI. *The basic salt* B_{1-1-2}. The investigation and the analysis confirmed the fact that this salt is the first product of the action of cold water on Z_{10}; also of cold dilute nitric acid containing less than 6 pCt. of N_2O_5 on Z_{10}; or of cold water on a not too acid solution of bismuth nitrate. It forms small scales, exceedingly thin crystalline plates without a definite shape and showing double refraction. They are not permanent when they remain in contact with the mother liquor but gradually become converted into another basic salt. It cannot even be dried over sulphuric acid without decomposition. No nitric acid is expelled but it loses water until 0.7 mol. of this is left. This behaviour is not yet explained since B_{1-1-1} does not lose water over sulphuric acid. The velocity of change and the composition of the basic salt both depend on the concentration of the mother liquor and the temperature. As such basic salts have been found: B_{1-1-1}, B_{10-9-7}, $B_{6-5-8(9)}$. It has not yet been ascertained at what dilution and temperature between 20° and 75° the formation of B_{1-1-2} by the action of water on Z_{10} ceases and B_{1-1-1} is formed (or B_{10-9-7} or B_{6-5-8}).

VII. *The basic salt* B_{1-1-1}. This salt is formed from B_{1-1-2},

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[1]) L = Solution, G = Vapour.

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when this remains in contact with a solution containing more than 1 pCt. N_2O_5. If the nitric acid amounted to a few percent only the change required some months at the ordinary temperature. When a few more percent were present the time was reduced to a few weeks. The more the strength of the acid approaches the point where the existence of Z_{10} becomes possible, namely 24.83 pCt. of N_2O_5 with 32.9 pCt. of Bi_2O_3 at 20°, the more quickly the change will take place. For instance, if it contains 21 pCt. (with 27.15 pCt. of Bi_2O_3) the change only takes a few hours at 20° [1]). At higher temperatures — between the limits 9° and 75° — the change proceeds proportionally more rapidly.

The crystals thus formed are probably monoclinic and have an angle of extinction of 10°—15°. Their composition was determined by analysis, which had not been done as yet.

When Z_{10} decomposes at 75.5°, the same salt is formed, but it then has another crystalline form. It forms hexagonal thin prisms which are apparently isotropic but extinguish to the right if they lie on a side plane (salt β). Analysis gave the composition B_{1-1-1}. It is also formed, together with the first form (salt α), at lower temperatures, such as 65°, from Z_{10} and a solution. The salt β seems to be more stable than the salt α; since in a solution from which the salt α had first deposited, this was after some time converted into the salt β, the liquid having undergone no perceptible change in composition [2]).

VIII. *The basic salt* $B_{6-5-9(8)}$. This salt is formed (as shown by very concordant analyses) at the ordinary temperature from B_{1-1-2}, when this remains for some months in contact with a very dilute solution ($<$ 1 pCt. of N_2O_5 and $<$ 0.33 pCt. of Bi_2O_3).

It also crystallises out when Z_{10} is decomposed by water, and the solid salt which is formed is dissolved in much water. This solution after a short time deposits $B_{6-5-9(8)}$. Even when the scales (B_{1-1-2}) are left for a long time over water so that they attract moisture and become covered with a layer of liquid, this salt is gradually formed. In one experiment, they were completely converted after the lapse of one year [3]).

The crystals are bi-axial, optically negative and belong to the

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[1]) The crystals of B_{1-1-2} were shaken in a shaking-apparatus with the solutions for 5 hours.

[2]) Some difference must exist, though a very small one.

[3]) For instance, a dilution obtained by adding 1 part of Z_{10} to 24 parts of H_2O.

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rhombic system and consequently extinguish to the right. Placed over sulphuric acid they behave like B_{1-1-1} losing neither nitric acid nor water.

They are also formed at higher temperatures from B_{1-1-2} or B_{1-1-1}, even when the solution is still more concentrated, but they then appear as small right — angled rhombic crystals. They are very stable, for they may be boiled for a considerable time with water without losing their transparency. A portion, however, dissolves but again deposits on cooling as $B_{6-5-9(8)}$. Larger crystals of the same composition are also formed. When heated for some hours on the boiling waterbath, the crystals become opaque; they have then disaggregated to a minute crystalline powder of B_{2-1-1}.

The number of mols. of water in the salt $B_{6-5-9(8)}$ is not yet quite fixed. It varies from 8—9 and it remains possible that there exist two hydrates with 8 and 9 mols. of H_2O respectively, and that this may account for the small difference in the crystalline form noticed in different preparations. A further investigation must decide.

IX. *The basic salt* B_{10-9-7}. This compound is nearer to B_{1-1-1} than the preceding one. By treating Z_{10} with water a salt answering to this composition was obtained occasionally. The crystals extinguish to the right like B_{6-5-8}, but still they make another impression; they also exhibit a weaker double-refraction.

On treating Z_{10} with warm water, not only $B_{6-5-9(8)}$ but also B_{1-1-1} and B_{10-9-7} made their appearance and this appeared to depend on the quantity of water present.

B_{1-1-1}	with	a	quantity	of	1—about	3parts	of	water	to	1part	of	Z_{10}		
B_{10-9-7}	»	»	»	»	about3—	»	20	»	»	»	»	»	»	»
$B_{6-5-8(9)}$	»	»	»	»	20—25	or	more	»	»	»	»	»	Z_1	

An investigation was instituted to see whether B_{10-9-7} represented merely a state of transition between B_{1-1-1} and B_{6-5-8}, and whether crystals were obtainable which stood nearer to B_{1-1-1} or to B_{6-5-8}, but this investigation has not as yet given any positive results.

X. *The basic salt* B_{2-1-1}. As already stated above this salt was obtained in a crystalline condition as the final product of the action of boiling water on the neutral salt. This is in agreement with the experience of former investigators. The crystals were too small to permit their shape to be properly observed.

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XI. *The basic salt* B_{5-4-9}, B_{4-3-9}, B_{5-3-8}, B_{5-3-6} described by JANSSEN, BECKER, DUFLOS and HERBERGER do not exist. *Following their methods of preparation no other salt than* B_{6-5-9} (8), *could be obtained* as shown by the crystalline form and the analysis. As the analytical process used by these investigators was faulty as regards the nitric acid, we may assume that they have found too little nitric acid. By a too prolonged washing with hot water (DUFLOS and HERBERGER) they may have had to deal with mixtures of B_{6-5-9} and B_{2-1-1}. The said basic salts must therefore, be rejected as long as there is no better proof of their actual existence.

XII. *Magisterium Bismuthi.* The preparation of this pharmaceutical preparation is differently described in the pharmacopaea and chemical manuals and its composition is given wrongly. As all the pharmacopaea direct the decomposition of Z_{10} with about 20 parts of hot or boiling water, it cannot consist of B_{1-1-2} or B_{1-1-1}, but must contain B_{6-5-9} (8) or B_{10-9-7}, or a mixture of both, sometimes even B_{2-1-1}. An investigation showed that different Dutch pharmaceutical preparations answered to the composition B_{6-5-9} (8) and others to a mixture of this salt with B_{10-9-7}.

B. EQUILIBRIUMS IN THE SYSTEM [Bi_2O_3—N_2O_5—H_2O] WITH SOLID AND LIQUID PHASES.

The vapour phase has been altogether left out of consideration so that all results relate to the ordinary atmospheric pressure.

The course of the Isotherms, which indicate the composition of the liquid phases which were in equilibrium with the different solid phases, was totally or partially determined for three temperatures: 20°—30°—65°. Some few points were also determined at 9°, 11° and temperatures between 65° and 80°.

These isotherms ware graphically represented in the well-known manner in equilateral triangles; with the aid of these a regular prism was constructed, the length of which answers to the temperature axis [1]).

In this way a figure in space was formed of which I now present to the meeting a plaster cast, with the following perspective drawing of the same.

The triangle in the front surface of the figure corresponds to a

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1) The points at the angles of each equilateral triangle (therefore the long sides of the prism) answer to the compositions 100 parts of H_2O, 100 parts of N_2O_5, 100 parts of Bi_2O_3. (See figure.)

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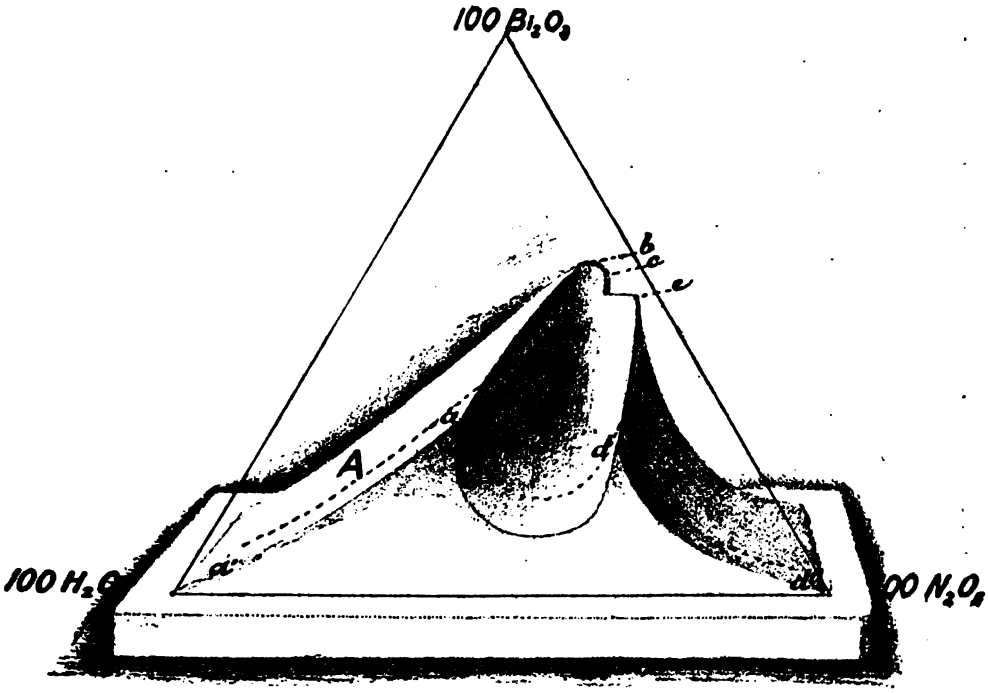
temperature of 9°. The point *b* which lies furthest-back is situated in the triangle of 75°.5. The equilibria of the system which are possible at these temperatures in the most dilute and the most concentrated solutions, and also the equilibria at temperatures below 9° and above 76° are as yet entirely wanting.



On the isotherm at 20°, the course of the branches was determined where the salts B_{6-5-9}, B_{1-1-2}, Z_{10} and Z_3 occur as solid phases in the system. In the figure it is shown by a dotted line. The branch with Z_{10} is determined at 30°, the branches with B_{1-1-1}, Z_{10} and Z_3 as solid phases are determined at 65°. The courses of two quadruple lines [1]) were also determined.

1. The one (*a b c* in the figure) which has the solid phases B_{1-1-1} and Z_{10} has been determined between the temperatures 9° (*a*) and 75°5 (*b*) and further back to 72° (*c*). This line shows a temperature maximum at 75°5, where Z_{10} is decomposed into B_{1-1-1} and liquid (p. 198). It then rebends itself. Its backward course has been examined up to 72° (*c* in the fig.).

2. The quadruple line which has the solid phases Z_{10} and Z_3

[1]) The quadruple lines separate the triple surfaces formed by the different isothermal curves of different temperatures.

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has been determined between 9° and 65° (points *d* and *e* in the fig.). The region of B_{1-1-1} (*A* in the fig.) between 9° and 75°5 has been to a great extent explored, but its boundary with the region B_{1-1-2} and of $B_{6-5-9(8)}$ is not yet known. The regions of B_{1-1-2} and of $B_{6-5-9\,(8)}$ are situated near the low concentrations. They partly cover or practically coincide with the region of B_{1-1-1} or with each other, because B_{1-1-2}, which is the more labile phase, can change in presence of the same liquid into the more stable phases B_{1-1-1} or B_{6-5-9}, which causes but very little change in the liquid phase.

The region of Z_{10}, as a solid phase (*B* in the fig.), has been explored between 9° and 75°5; except a small portion at the right of the figure between 65° and 72°, where the region is probably bounded by that of B_{1-2-2} and that of Z_4. The missing part lies between *c* and *e* as indicated in the figure by a right angle.

Of the region of Z_3 as a solid phase (*C* in the fig.) only a portion is known: 1st. because the quadruple line with Z_3 and Z_4 as solid phases, which must bound it on one side, has not yet been determined 2nd because it has not been determined how far the isotherms with Z_3 extend to the right. These have not been continued further than the point, where the liquid phase reaches the strength of 1 mol. of N_2O_5 on 1 mol. of H_2O. It remains possible that with solutions, which contain less water still, Z_3 is not capable of existence, but that a neutral salt with less than 3 mols. of H_2O, or an anhydrous salt or a salt with more than 3 mols. of N_2O_5 takes its place. In each case the region of Z_3 must end and pass into another one before the system is reached which consists entirely of $B_{t_2}O_3$ and N_2O_5 [1]).

From this it is evident that the solubility of B_{1-1-1} increases pretty regularly between the said temperatures with the amount of nitric acid in the liquid phase, but that it again slightly decreases after the temperature maximum of 75°.5. The solutions which are in equilibrium with B_{1-1-1} differ (as above mentioned) very little from those which belong to $B_{6-5-9(8)}$, at least at 20°. The solubility of Z_{10} between 9° and 75° first decreases rapidly with the increase of nitric acid in the liquid phase, then passes through a minimum and then again increases until Z_3 becomes the solid phase. The solubility of Z_4 decreases rapidly with the increase of the strength of the nitric acid. It is not known whether it also passes through a minimum.

[1]) These systems lie in the graphic representation on the right side plane of the regular triangular prism.

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The graphic representation of the experimentally found triple-planes and quadruple-lines in an equilateral triangle (in the well-known manner) allows of the prediction of quite a series of cases of equilibrium. So for example it may be concluded what will happen when a certain quantity of Z_{10} is treated at a certain temperature (within the observed limits) with increasing quantities of water, i.e. which solid phases are formed and what composition the liquid phase possesses. Also what will happen when a certain quantity of the basic salt B_{1-1-1} (with or without motherliquor) is treated with increasing quantities of nitric acid of a certain strength, or when the strength of the acid is increased. If may also be concluded which mixtures of B_2O_3, N_2O_5 and H_2O may lead at a certain temperature to the formation of one of two above mentioned solid phases, and which changes that mixture will undergo at increasing or decreasing temperatures. And so on.

The isothermal curves at temperatures above 75.5° are not yet determined. This determination will present great difficulties in its execution, particularly in the separation of the solid phases.

The agreement in form of the triple-lines in this system with those of [$HgO—SO_3—H_2O$] as determined by C. HOITSEMA (Zeitschr. physik. Chem. 1895, 17, 651) is worthy of notice.

Chemistry. — Prof. A. P. N. FRANCHIMONT presents to the library of the Academy the dissertation of Dr. L. VAN SCHERPENZEEL entitled: "*The action of hydrogen nitrate (real nitric acid) on the three toluic acids and some of their derivatives*", the contents of which he explains as follows:

The research of Dr. VAN SCHERPENZEEL is connected with that of Dr. MONTAGNE about which I reported last January and was undertaken at the same time. It required the knowledge of a twenty new compounds which have been prepared by Dr. VAN SCHERPENZEEL and are described in his dissertation.

Following up the researches of VAN ROMBURGH in 1885 and of TAVERNE in 1897 and 1898 on the action of nitric acid on benzoic acid and some of its derivatives, such as the methyl ester, the amide and both the methylamides, the question arose what influence would be excercised on the action of the nitric acid by the introduction of an atomic group in different positions into the benzene nucleus. Whilst MONTAGNE had chosen the monochlorinederivatives and thus

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introduced the negative element chlorine into the nucleus, VAN SCHERPENZEEL did the reverse and chose the monomethylderivatives with the positive group CH_3, which are isomeric with phenylacetic acid and its derivatives already investigated by TAVERNE.

It has been known since long that the temperature plays an important part in the action of nitric acid. VAN SCHERPENZEEL also found that at zero mononitrocompounds are always formed, whilst at the ordinary temperature dinitroderivatives are mostly produced, although the longer duration of the action in the second case also has a share in the result. TAVERNE had also obtained dinitro-substances with phenylacetic acid and its derivatives, whilst with benzoic acid only mononitroderivatives were formed, which according to MONTAGNE is also the case with the three monochloro-benzoic acids.

The suitability of real nitric acid as a nitrating agent was also again demonstrated here by the easy formation of the dinitrocompounds without any oxidation.

The influence of the groups OH, OCH_3, NH_2, $NHCH_3$ and $N(CH_3)_2$ on the nitration of the benzene residue was shown to be the strongest in the case of those containing nitrogen. With ortho- and meta toluic acid and their derivatives, where two isomeric nitro-compounds are generated, the amount of that which is obtained as a bye-product is much increased. In not a single case, however, was the influence of the different groups of such a nature that the nitro-group took up a position other than in the case of the free acid.

It deserves attention that in the case of the dimethylamides of the three toluic acids no second nitro-group entered the benzene nucleus even if they were exposed for 24 hours at the ordinary temperature to the action of the nitric acid, whilst those of phenylacetic acid and phenylpropionic acid yielded, according to TAVERNE, dinitro-acid.

The following facts were noticed as regards the influence of the itrated acid-residues on the nitrogen-containing groups. At zero, neither the amides nor the methyl derivatives were decomposed. At the ordinary temperature only the amides and monomethylamides but not the dimethylamides were decomposed; the latter yielded the dimethylamides of the mononitro-acids whilst the others were decomposed and yielded dinitro-acids.

Stable methylnitramides were not obtained. There exist, therefore, great differences between the derivatives of benzoic acid, of the three chlorobenzoic acids, of phenylacetic and phenylpropionic acid and those of the toluic acids; these differences may be reduced to their true dimens-

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ions by means of more accurate determinations keeping account of the temperature and time of action. If the present results are accepted, the nitrotoluic acids which are mentioned now ought to be comparable with trichloracetic acid. This is, however, an extraordinarily strong acid, according to the affinity constant, which is not to be expected of the nitrotoluic acids, the constant of which does not seem to have been determined as yet. Again, according to the affinity constant, benzoic acid is a weak acid which, excepting one case, becomes still weaker by the introduction of a methyl group; para- and meta-toluic acid, also phenylacetic acid are weaker, but for orthotoluic acid an affinity constant twice as great as that of benzoic acid is recorded. Although by the introduction of the nitrogroup, particularly in orthoposition to the carboxyl group, the strength of the acid is much increased — the affinity constant of orthonitrobenzoic acid is more than a hundred times larger than that of benzoic acid — this cannot cause the strength of the nitro-acids to equal that of trichloracetic acid. There remains further the strange fact that no difference has been noticed between the isomeric nitrotoluic acids although great differences were to be expected.

From all this appears that the observed facts cannot be explained simply by the negativeness of the acid-residue, but that other causes take part in the matter as has been found repeatedly former similar cases.

VAN SCHERPENZEEL regards the nitro-o-toluic acid melting at 145°, prepared by JACOBSON and WIERSS as a mixture and attributes the same composition, namely 6 nitro-o-toluic acid (CH_3 at 1), to the acid which he has isolated from this mixture by converting it into the methylesters, selecting their crystals and saponifying them; it melts at 184°—184°.5.

The reasons for his opinion are as follows:

It is formed together with the acid which has the nitrogroup at 4 and it not only differs from this but also from those where the nitrogroup stands at 3 and 5. The position 6 is after 4 the most favorable for the introduction of the nitrogroup, namely meta to the carbonyl group, and ortho to the CH_3. On further nitration the same dinitro-acid is produced which is formed from the 4 mononitro-acid.

The as yet unknown dinitro-m-toluic acid now obtained by VAN SCHERPENZEEL has been given by him the formula 4.2 (CH_3 at 1) because the two preceding mononitro-acids are 4 and 2 and also

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because it is the most probable, since the nitrogroup does not readily take up the paraposition in regard to carboxyl during nitration.

This acid gives a violet coloration with alkalis, the colour changing gradually into dark red, a phenomenon observed also in other nitro-compounds and described by V. MEYER, LOBRY DE BRUYN, HANTZSCH and others. It is remarkable that 2.6 dinitro-p-toluic acid and 4.6 dinitro-o-toluic acid did not give this reaction although from the position of the nitro-groups they might have been expected to do so.

VAN SCHERPENZEEL finally noticed a very peculiar property of the dimethylamide of 4 nitro-metatoluic acid prepared by means of dimethylamine from the chloride of that acid. The colourless thick crystals on being exposed to light, more rapidly in direct sunlight, assumed a red colour which is not superficial as may be proved by rubbing them to powder and examining the fine particles under the microscope. The colour does not disappear when the substance is kept in the dark at the ordinary temperature, but on being repeatedly recrystallized colourless crystals are always obtained which again turn red on exposure to light. This phenomenon somewhat resembles that to which MARCKWALD has given the name "Phototropy". It is remarkable, however, that when the same compound is prepared in another way, namely by nitrating the dimethylamide of m-toluic acid it does not show this phenomenon; this would indicate the presence of an unremovable impurity, but no proof could be given of its existence.

He, therefore, prepared the chloride of o nitrobenzoic acid and from this the as yet unknown dimethylamide melting at 78°. This also turned red on exposure to light although not so strongly.

After remarking that the dimethylamides used in his experiments were more soluble in water than the monomethylamides and that the latter were again more soluble than the amides, he gives in the annexed table the melting points of the substances mentioned. They exhibit few deviations from the ordinary regularities. It is a peculiar fact that whilst the melting points of nearly all the derivatives of 4 nitro-o-toluic acid are situated higher than those of their isomers, the acid itself and its chloride have lower melting points:

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Melting points.

	Acid.	Methylester.	Chloride.	Amide.	Methyl-amide.	Dimethyl-amide.	Nitrile.
p. toluic acid.	179°	34°	—1°5	159°5	145°—145°5	41°	29°5
m. toluic acid.	110°	—4°	—23°	93°—94°	44°5—45°	liq.	—23°5 to —23°
o. toluic acid.	102°5—103°	—54° to —51°	—	138°5	75°	liq.	—13°
2 nitro. p. toluic acid.	188°5—189°	49°	—	166°—166°5	149°	49°5 ?	—
4 nitro. m. toluic acid.	223°	72°5	—	191°	135°—136°	88°5	—
2 nitro. m. toluic acid.	184°—185°	—	—	135°5—136°	—	—	—
4 nitro. o. toluic acid.	178°—178°5	69°	59°—60°	173°—174°	160°	105°5—106°	—
6 nitro. o. toluic acid.	184°—184°5	66°	68°—68°5	163°	131°—132°	69°5—70°	—
2.6 dinitro. p. toluic acid.	159°	—	—	—	—	—	—
2.4 dinitro. m. toluic acid.	173°	104°—105°	—	—	—	—	—
4.6 dinitro. o. toluic acid.	206°	73°—74°	—	—	—	—	—

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Chemistry. — "*Thermodynamics of Standard-Cells*" (3rd Part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. It is my intention, in this communication, to apply the previously developed theory to the WESTON-cadmiumstandard-cell and to show that it is also here in perfect agreement with experiment. In the first place the mechanism of the reaction will be more closely considered.

The cell is constructed [1]) as follows:

$Hg—Hg_2SO_4$— saturated solution of cadmium sulphate—cadmium amalgam (14,3 pCt. of Cd.)

We must notice here, as I have already said in my second communication, that cadmium amalgam does not behave in the same way as pure cadmium. The measurements of HOCKIN and TAYLOR [2]) and those of JÄGER [3]) have plainly proved this. The following table taken from JÄGER's communication shows this:

TABLE I.

Composition of the amalgam.		E.M.F. against the 14.3 percent Cd amalgam (Volt.)
% Cd.	Cd: Hg.	
1	1 : 100	— 0.021
2	2 : 100	— 0.013
5	5.3 : 100	nearly 0
10	11.1 : 100	0
11.4	12.9 : 100	0
13.0	15.0 : 100	0
14.3	16.7 : 100	0
15.4	18.2 : 100	0 up to + 0.001
20.0	25.0 : 100	+ 0.001 up to + 0.011
Cd. amalgamated.		0 to about + 0.044
Cd. pure.		+ 0.051

up to $^1/_{100}$ millivolt

gradually rising.

[1]) JÄGER and WACHSMUTH, WIEDEMANNS Annalen 59, 575 (1896).

[1]) Journal of the Society of Telegraph-Engineers, VIII p. 282 (1879).

[2]) WIEDEMANNS Annalen, 65, 106 (1898).

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When 2×96540 Coulombs pass through the cell, then

a. 1 gram atom of Cd will be withdrawn from the cadmium amalgam (Heat effect W_1)

b. the liberated Cd will combine with the SO_4 of the Hg_2SO_4 to $CdSO_4$ (Heat effect W_2),

c. which will then abstract water from the saturated solution of cadmium sulphate and form $CdSO_4 . {}^8/_3 H_2O$ (Heat effect W_3). This salt will deposit in the saturated solution.

The said abstraction of water will take place according to the equation:

$$CdSO_4 + \frac{{}^8/_3}{A - {}^8/_3} CdSO_4 . AH_2O = \frac{A}{A - {}^8/_3} CdSO_4 . {}^8/_3 H_2O. \quad . \quad . \quad (1)$$

in which A represents the number of mols. of water associated with 1 mol. of $CdSO_4$ in the saturated solution at the temperature of the cell.

2. The total heat effect in the cell on the passage of 2×96540 Coulombs is now:

$$W_1 + W_2 + W_3 \text{ calories.}$$

The heat of formation of $CdSO_4$ and Hg_2SO_4 are known and amount to respectively 219900 and 175000 calories.

The heat evolved when 1 gram atom of Cd is withdrawn from the amalgam (W_1) has been experimentally determined by me (see below) whilst the quantity of heat (W_3) evolved by the process represented in equation (1) may be deduced from the thermochemical determinations of THOMSEN, taken together with those of Mr. H. B. HOLSBOER which he has kindly placed at my disposal.

a. Experimental determination of the Heat evolution (W_1) *which takes place on the withdrawal of* 1 *gram atom of cadmium from the* 14.3 pCt. Cd *amalgam.*

3. I have not determined this heat effect by thermochemical, but by electrochemical means by a method which in a case like this deserves the preference on account of its very great accuracy [1]).

For this purpose I constructed a cell according to the following scheme:

Cd - dilute solution of cadmium sulphate of arbitrary concentration - 14.3pCt. Cd amalgam.

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[1]) Compare RICHARDS and LEWIS, Proc. Americ. Acad. of Arts and Sciences. Vol. XXXVI, 87. Dec. 1898. Zeitschr. für phys. Chemie 28.1 (1899).

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When in such a cell the current is closed, Cd will pass from the cadmium electrode to the amalgam.

If we apply to this cell the well-known equation of GIBBS and VON HELMHOLTZ.

$$E = \frac{E_c}{n\varepsilon_o} + T\frac{dE}{dT} \quad \ldots\ldots\ldots \quad (2)$$

we can find E_c by the determination of the E. M. F. of the cell and its temperature coefficient and this quantity is simply the amount of heat evolved when 1 gram atom of cadmium is added to the amalgam, in other words, the quantity of heat which we wish to determine but with the opposite sign.

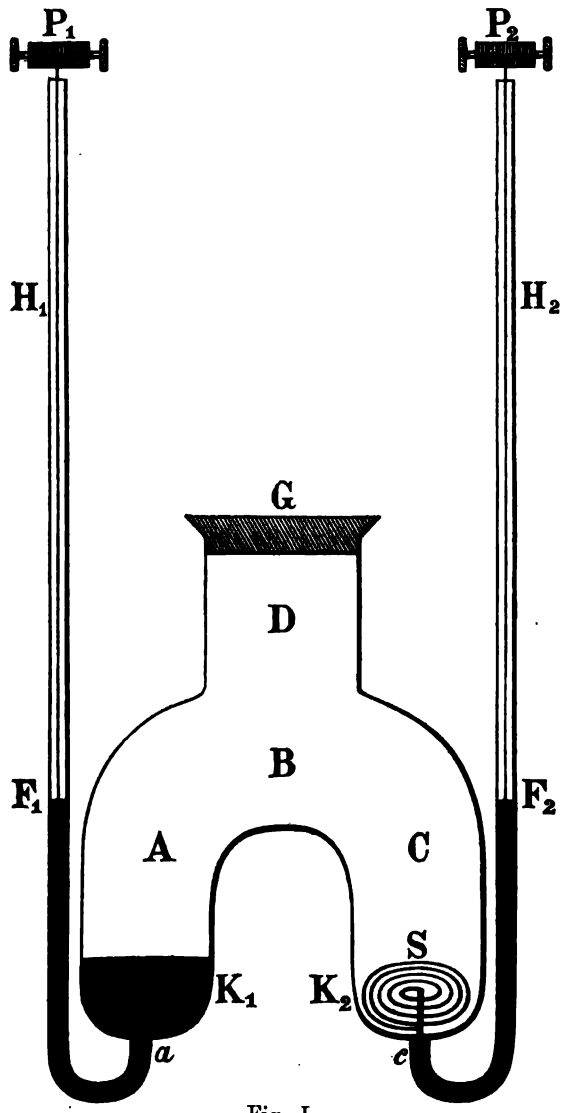

Fig. I.

4. The cell used had the form indicated. The capillaries F_1 and F_2 are sealed to the arms A and C of the vessel ABC. The capillary F_1 communicates with A but F_2 on the other hand is closed at the spot where it is sealed to C and admits a platinum wire which in C is wound up to a spiral S and projects into F_2 about 1 cm.

Into A is poured the amalgam (14.3 pCt. of cadmium) which is in direct contact with the platinum wire H_1, which runs into A.

Into C is introduced metallic crystalline cadmium so as to quite surround the platinum spiral S. Into F_2 mercury is poured which forms the contact between S and the platinum wire H_2.

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5. The metallic crystalline cadmium was prepared as follows [1]: 200 grams of crystallized cadmium sulphate were dissolved in warm water precipitated with ammonia and redissolved in a slight excess of the same. After diluting to 600 cc., the liquid was electrolyzed between two platinum electrodes of 55 cm^2. surface at a tension of 6—8 volts and with a current of 4—5 ampères. Splendid dendritic crystals of Cd are deposited at the negative electrode which are left in the liquid until enough of the metal has separated.

The crystalline metal is first washed a large number of times with very dilute sulphuric acid, then with the same solution of cadmium sulphate which serves afterwards in the cell $Cd - CdSO_4$ Cd-amalgam. The solution, the concentration of which may be chosen at will, was prepared by dissolving 200 grams of crystallized cadmium sulphate in 500 cc. of water [2].

The metallic cadmium after being well washed (reaction with congo-red) was kept in this solution; the electrodes thus prepared are electrically well-defined and different preparations only showed a mutual potential difference of 0.00001 volt.

6. The cadmium amalgam of 14.3 pCt. was prepared by weighing the respective quantities of the components. In the metallic cadmium from MERCK no impurities could be detected by analytical means and the test recommended by MYLIUS and FUNK [3] which shows 0.01 pCt. of zinc with certainty also gave a negative result.

The mercury was purified with mercurous nitrate and then distilled twice in vacuo.

7. After the electrodes in the cell fig. 1 were put in their place, the above mentioned solution of cadmium sulphate (which was far from saturation even at 0°) was poured in and the cell closed by means of an india-rubber stopper, *g*.

The length of the capillaries renders it possible to completely immerse the whole cell in a thermostat.

The E.M.F. of this cell of which I first constructed 2 specimens for control (I and III) was determined at 0°.0 C. and 25°.0 C.

The cells were kept at zero in a thermostat consisting of a copper cylinder isolated with cotton-wool and containing a mixture of finely

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[1]) Compare RICHARDS and LEWIS, Proc. Amer. Acad. Arts and Sc., Vol. XXXIV, p. 87, Dec. 1898. Zeltschr. phys. Chem. 28, 1 (1899).

[2]) The water was the same as used for determinations of the electrical conductivity and consequently very pure.

[3]) Zeitschr. anorg. Chem. 13, 157 (1897).

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crushed ice and water. Only by vigorously stirring with three screw propellers fixed at different heights in the cylinder and kept in rotation by a HEINRICI hot-air motor, was it found possible to maintain in every part of the thermostat an equal temperature [1]) of 0°.

The thermometer used was divided in $^1/_{10}°$ and compared with a standard instrument from the Physikalisch-Technische Reichsanstalt at Charlottenburg.

At 25°,0 C. the temperature was regulated with a toluene-regulator within 0°,03 C.

The E.M.F.'s were measured, by means of POGGENDORFF's compensation method. A THOMSON's mirror galvanometer was used as the zero instrument, a small accumulator as the working cell and a WESTON-cell and two CLARK-cells as standards.

The WESTON and the CLARK-cells stood in the thermostat at 25°,0 C. (also in the experiments at 0°) [2]). After each measurement the accumulator was tested by means of the WESTON-cell.

8. In the first place, I determined the relation between the E.M.F. of the WESTON-cell and of both the CLARKS *A* and *B*.

$^2/_{6}{}^{00}$ $\quad \frac{\text{CLARK } A_{25°}}{\text{WESTON }_{25°}} = 1.3942 \qquad \frac{\text{CLARK } B_{25°}}{\text{WESTON }_{25°}} = 1.3942.$

If we take as the E.M.F. of the CLARK-cell at 25°,0 1.4202 Volt then that of the WESTON-cell at 25°,0 = 1.0185 Volt whilst in the Reichsanstalt 1.0184 Volt has been found at this temperature.

9. The E.M.F.'s of the cells I and III were then determined at 25°,0 C. and 0°,0 C.

TABLE II.

Electromotive force at 25°.0 C. of the cell
Cd—$CdSO_4$ solution — Cd-amalgam 14.3 % Cd. in Volts.

	Date	No. I.		Date	No. III.
$^2/_{6}{}^{00}$	4.00 p.m.	0.04998	$^5/_{6}{}^{00}$	8.45 p.m.	0.04989
	4.30	0.04995			
	5.10	0.04999			
$^4/_{6}{}^{00}$	12.25 p.m.	0.04995			
		averge 0.04997			averge 0.04989

[1]) The method so frequently used for the testing of thermometers of placing these instruments in a funnel with crushed ice, seemed to me to be untrustworthy as differences in temperature up to 0°.3 C. were observed.

[2]) Proc. Nov. 25, 1899, p. 290.

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At 0°,0 C. the following was found:

TABLE III.

Electromotive force at 0°.0 C. of the cell
Cd—$CdSO_4$ solution — Cd. amalgam 14.3 % Cd. in Volts.

	Date	No. I.		Date	No III.
2/6 00	1h.50 p.m.	0.05571	5/6 00	4h.50 p.m.	0.05571
	2h.25	0.05571		5h.24	0.05581
	2h.50	0.05571			
4/6 00	11h.15 a.m.	0.05591			
	11h.50	0.05591			
	average	0.05579		average	0.05576

We, therefore, find as the mean of the observations with both the cells:

$$\text{E.M.F. at } 25°0, \text{ C.} = 0{,}04993 \text{ Volt.}$$
$$\text{E.M.F. at } 0°{,}0 \text{ C.} = 0{,}05577 \text{ „}$$

The temperature coëfficient of the E.M.F. is therefore on the average

$$\frac{0{,}04993 - 0{,}05577}{25} = -\ 0{,}000233 \text{ Volt.}$$

10. On this result I had a check [1]), which was very welcome to me. JÄGER [2]) has determined the E.M.F. of a similar cell and has found 0,051 volt, but he has not given the temperature at which his determination was made. I have now calculated from my determinations the temperature at which E would be 0,051 volt according to my observations. I find from

$$E_t = E_{25} + (25 - t)\ 0{,}000233$$
$$t = 20°\text{C.}$$

In reply to my inquiry, Prof. JÄGER was kind enough to state that he had indeed made his observations at about 20° C.

---

[1]) Subsequent experiments proved to me the correctness of the supposition that the temperature coefficient between 0° and 25° does not alter with the temperature.

[2]) WIEDEMANNS Annalen, 65, 106 (1898).

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11. If we now introduce the values of E and $\frac{dE}{dT}$ found, into the equation 2 on page 210 and calculate E_c for 18° C., we find:

$$(E_{291} = 0{,}0515\,;\ \frac{dE}{dT} = -\ 0{,}000233\,;\ T = 291)$$

$$E_c = 2\,(0{,}0515 + 291 \times 0{,}000233) \times 2278\text{?} \text{ calories} = +\ 5436 \text{ calories.}$$

The heat effect of the withdrawal of 1 gram atom of *Cd* from the 14.3 pCt. *Cd* amalgam is therefore,

$$W_1 = -\ 5436 \text{ calories}\ ^{1}).$$

β. Determination of the Heat effect W_3.

12. We have still to determine the heat effect which accompanies the change:

$$CdSO_4 + \frac{^8/_3}{A - ^8/_3}\ CdSO_4 .\ AH_2O = \frac{A}{A - ^8/_3}\ CdSO_4 .\ ^8/_3\ H_2O.$$

The factor A (see page 209) may be taken from the solubility determinations of MYLIUS and FUNK[2]) and KOHNSTAMM and COHEN[3]), who have found quite identical figures.

---

[1]) In my second communication on the thermodynamics of the standard-cells (these Proceedings 26 May 1900 pag. 36) it was concluded from older and newer statements in the literature that the abstraction of 1 gram atom of zinc from the zinc-amalgam of the CLARK-cells took place without any heat effect. That such is really the case is taught by the following experiment:

I constructed a cell according to the scheme:

$$\underset{1\,:\,9}{\text{Zn amalgam}}\ -\ \underset{\text{dilute}}{ZnSO_4 \text{ solution}}\ -\ \text{Zn}$$

just in the same manner as described above for the *Cd*-cells. Of this cell the E.M.F. was determined at 0°,0 C. and 25°,0 C. There was found at:

0°,0 C.	0,000488 Volt.
25°,0 C.	0.000570 "

$$\text{therefore } \frac{dE}{dT} = +\ 0{,}00000328 \text{ Volt.}$$

From this follows: $E_c = 2\,(0{,}00048 - 273 \times 0{,}00000328)\,22782$ calories

$$E_c = -\ 9 \text{ calories.}$$

The quantity of heat required, is therefore + 9 calories or practically nil.

[2]) B. B. 30, 824 (1897).

[3]) WIEDEMANNS Annalen 65, 344 (1898).

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At 18°C., A = 15,17.

The equation representing the change therefore becomes at this temperature:

$CdSO_4 + 0{,}212\ (CdSO_4.\ 15{,}17\ H_2O) = 1{,}212\ CdSO_4.\ ^8/_3\ H_2O$ . . (3)

If the systems to the left and the right of the sign of the equality are dissolved in so much water, that both have the concentration $CdSO_4$—400 H_2O, we can find the quantity of heat W_3 (p. 209) from the heat effects so obtained.

I now reproduce the following from the data put at my disposal by Mr. HOLSBOER:

Heat of dilution	$CdSO_4.\ 13{,}6\ H_2O$	to $CdSO_4.\ 30\ H_2O$	$= +\ 1034$ calories.
„	$CdSO_4.\ 15{,}6\ H_2O$	„ $CdSO_4.\ 20{,}6\ H_2O$	$= +\ 405$ „
„	$CdSO_4.\ 20{,}6\ H_2O$	„ $CdSO_4.\ 30{,}6\ H_2O$	$= +\ 285$ „
„	$CdSO_4.\ 30{,}6\ H_2O$	„ $CdSO_4.\ 50{,}8\ H_2O$	$= +\ 231$ „
„	$CdSO_4.\ 50\ H_2O$	„ $CdSO_4.\ 100\ H_2O$	$= +\ 220$ „
„	$CdSO_4.\ 100\ H_2O$	„ $CdSO_4.\ 200\ H_2O$	$= +\ 171$ „
„	$CdSO_4.\ 200\ H_2O$	„ $CdSO_4.\ 400\ H_2O$	$= +\ 108$ „

From this I calculate:

H. o. d.	$CdSO_4.\ 15{,}17\ H_2O - CdSO_4.\ 20{,}6\ H_2O$	$= \frac{405}{5} - 0{,}43 + 405$	$= +\ 440$ calories.
„	$CdSO_4.\ 20{,}6\ H_2O - CdSO_4.\ 30{,}6\ H_2O$	$=$	$= +\ 285$ „
„	$CdSO_4.\ 30{,}6\ H_2O - CdSO_4.\ 50\ H_2O$	$=$	$= +\ 222$ „
„	$CdSO_4.\ 50\ H_2O - CdSO_4.\ 400\ H_2O$	$=$	$= +\ 499$ „
	Heat of dilution $CdSO_4.\ 15{,}17\ H_2O - CdSO_4.\ 400\ H_2O$		$= +1446$ „

The heat of solution of $CdSO_4$—$CdSO_4.\ 400\ H_2O = +\ 10740$ calories (THOMSEN, Thermochem. Untersuchungen III, S. 201), and the the heat of solution of $CdSO_4.\ ^8/_3\ H_2O$—$CdSO_4.\ 400\ H_2O = +\ 2660$ calories.

The heat effect (W_3) which accompanies the change represented in equation (3) is therefore:

$$W_3 = 10740 + 0{,}212 \times 1446 - 1.212 \times 2660 = +\ 7822 \text{ calories.}$$

13. The heat evolved at 18° C. in the WESTON-cell at a passage of 2×96540 Coulombs may now be calculated:

$$E_c = W_1 + W_2 + W_3 = -\ 5436 + (219900 - 175000) + \\ + 7822 = +\ 47286 \text{ calories.}$$

14. This quantity must now be compared with that obtained

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from the direct observations of the E.M.F. of the WESTON-cell by JÄGER and WACHSMUTH [1]):

From their measurements it follows that the E.M.F. at t^0 is represented by the equation:

$$E_t = 1{,}0186 - 0{,}000038\,(t-20) - 0{,}00000065\,(t-20)^2 \text{ Volt.}$$

therefore: $E_{18^0} = 1.0186$ Volt.

$$\left(\frac{dE}{dT}\right)_{18^0\,\text{C.}} = -\,0{,}0000354 \text{ Volt.}$$

or $E_c = +\,47880$ calories

whilst the thermodynamic calculation gave $E_c = +\,47880$ calories.

The agreement between theory and experiment is, therefore, very satisfactory.

15. I will not neglect to point out that the idea hitherto prevailing on the mechanism of the change and which was represented by the equation:

$$Cd + Hg_2\,SO_4 \rightleftarrows 2\,Hg + CdSO_4$$

would here also lead to quite wrong results.

From the above it appears that we may represent the mechanism of the change which occurs in the WESTON-cell by

$$Cd \text{ amalgam} \rightleftarrows Cd + Hg\ ^2)$$

and

$$Cd + \frac{^8/_3}{A - ^8/_3}\,(\underset{\text{liquid}}{CdSO_4\,AH_2O}) + Hg_2SO_4 \rightleftarrows 2Hg + \frac{A}{A - ^8/_3}\,\underset{\text{solid}}{CdSO_4.\,^8/_3\,H_2O}$$

Amsterdam, University Chem. Lab.
June 1900.

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[1]) WIEDEMANNS Annalen 59. 575 (1896).

[2]) This provisional equation only represents the change of the amalgam *qualitatively*. The exact *quantitative* equation can only be given when the behaviour of the cadmium amalgam has been more exactly studied. (See my next paper on the metastability of the WESTON-cell).

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Chemistry. — "*The metastability of the Weston-Cadmiumcell and its insuitability as Standard of electromotive force*". By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. As is well known the CLARK-cell is inconvenient for accurate measurements on account of its great temperature coefficient (1 millivolt degree). For a number of years JÄGER and WACHSMUTH of the Physikalisch-Technische Reichsanstalt have been engaged with the study of a cell which does not suffer from this drawback. As is known, the result of their investigations has been [1]) that in 1896 they proposed to employ the cadmium cell of WESTON in a somewhat modified form as a standard.

This cell, constructed according to the scheme:

Cadmium amalgam (14.3 pCt. of Cd) — saturated solution of cadmium sulphate — Hg_2SO_4—Hg

possesses, according to their communications, all the good qualities of the CLARK-cell as regards constancy and ease of construction, but its temperature coefficient is 25 times smaller than that of the CLARK-cell.

The change of the E.M.F. amounts to only $^4/_{1000}$ pCt. per degree centigrade whilst that of the CLARK-cell is $^1/_{10}$ pCt.

Thermostats become superfluous even when very accurate measurements are required, which is a fact of some importance when it is considered that standard cells are much used for industrial purposes.

2. The connection between the E.M.F. and the temperature was determined by JÄGER and WACHSMUTH. They found (between 0° and 26°).

$$E_t = E_{20} - 3.8 \times 10^{-5}(t-20) - 0.065 \times 10^{-5}(t-20)^2,$$

but they observed at the same time that some cells did not follow this curve but showed certain irregularities at low temperatures; these cells had a much greater E.M.F. (about 1 millivolt) than the others.

In view of these deviations, Mr. KOHNSTAMM and I, in 1898, made a closer study of the behaviour of cadmium sulphate and found [2]) that the temperature coefficient of the solubility of $CdSO_4 . {}^8/_3 H_2O$ undergoes a sudden change at 15°.

Solubility determinations which were executed with many precautions gave the following result.

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[1]) WIEDEMANN's Annalen, 59. 575 (1896).

[2]) WIEDEMANN's Annalen, 65, 344 1898).

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TABLE I.

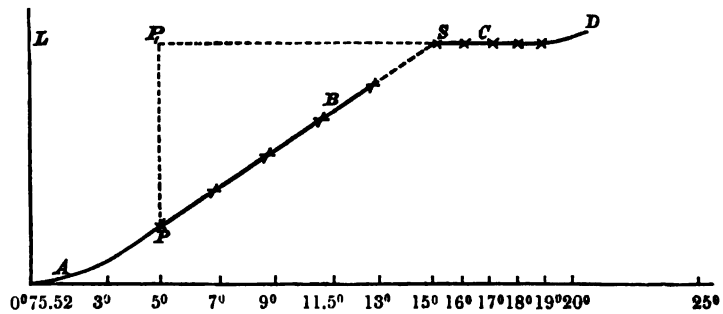
Temperature.	Grams of $CdSO_4$ dissolved in 100 grams of water. I.	II.	III.	Average.
0°0	75.52	—	—	75.52
5°0	75.69	75.61	—	75.65
7°0	75.73	—	—	75.73
9°0	75.84	75.87	—	75.85
11°5	75.98	75.90	—	75.94
13°0	76.00	76.07	—	76.04
15°0	76°11	76.14	76.09	76.11
16°0	76.16	—	—	76.16
17°0	76.14	76.12	—	76.13
18°0	76.13	76.15	—	76.14
19°0	76.18	76.18	—	76.18
25°0	76.82	76.78	76.84	76.79

The accuracy could be controlled by determinations which MYLIUS and FUNK had made in the Reichsanstalt at the same time. The following table contains a comparison of the results.

TABLE II.

Temperature.	In 100 grams of water dissolve grams of $CdSO_4$. MYLIUS and FUNK.	KOHNSTAMM and COHEN.
0°	75.47	75.52
10°	76.00	75.90
15°	76.06	76.11

Figure I represents the progressive change of the solubility.



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At about 15° C. the $CdSO_4 . {}^8/_3 H_2O$ must, therefore, undergo a change. This change has been already proved by means of the dilatometer [1]).

The deviations found by JÄGER en WACHSMUTH in the E.M.F. were explained by assuming that $CdSO_4 . {}^8/_3 H_2O$, the solubility of which is represented by the curve *SCD* remains, as a rule, somewhat obstinately in the metastable condition. A smaller E.M.F. of the WESTON-cells then corresponds to the greater solubility of the metastable phase (curve P_1S). If the salt passes into the stable modification (curve *APBS*), the solubility is lowered and the E.M.F. of the cells in which that modification exists is raised.

No objections to this view have been raised since the appearance of our paper; on the contrary in his publication on deviations noticed by himself in the behaviour of cadmium-cells, BARNES [2]) accepts our view. I will however, not neglect to point out that it always astonished me that such a small difference in solubility as represented by the points P and P_1 should lead to such an important difference in E M.F.

At the end of our paper we concluded that the WESTON-cell in the form used at the Reichsanstalt, i.e. containing the solid salt $CdSO_4 . {}^8/_3 H_2O$, should not be used below 15°, if the risk of having a cell which considerably deviates from the temperature formula given by JÄGER and WACHSMUTH is to be avoided.

3. My investigations on the thermodynamics of the standard cells made me return to the WESTON-cell which was now extensively studied in another direction.

In the following lines, I wish to give a summary of this investigation.

4. In order to find the heat-effect caused by the withdrawal of 1 gram-atom of Cd from the 14.3 pCt. cadmium amalgam used in the WESTON-cells, I constructed (see previous paper pg. 208) a number of cells of the type: Cd—dilute solution of cadmium sulphate — Cd-amalgam 14.3 pCt. The solution of cadmium sulphate was not saturated at 0°,0 C., so that no crystals could be deposited at that temperature. The details of the construction of the cells together with the precautions taken in view of impurities contained in the

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[1]) l. c.

[2]) Journ. of physical Chemistry, May 1900.

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materials have been fully described by me in my third communication on the thermodynamics of the standard cells (see communication (p. 208).

The E.M.F.'s of cells I, II and III at 0°,0 C. and 25°,0 C. were determined by POGGENDORFF's method as described in the paper already referred to.

The WESTON-cell and the CLARK cells which served as standards were always kept in a thermostat at 25°,0 C. In this way I found:

TABLE III.

At 25°.0 C.

No. I.		No. II.		No. III.	
Date	E.M.F. in Volt.	Date	E.M.F. in Volt.	Date	E.M.F. in Volt.
$^2/_6{}^{oo}$ 4h. p.m.	0.04998	$^2/_6{}^{oo}$ 4h.0 p.m.	0.04999	$^5/_6{}^{oo}$ 3h.45 p.m.	0.04989
4 30	0.04995	4 30	0.04992		
5 10	0.04999	5 10	0.04992		
$^4/_6{}^{oo}$ 12 25 p.m.	0.04995	$^4/_6{}^{oo}$ 12 25	0.04995		
average	0.04997 Volt.	average	0.04992 Volt.	average	0.04989 Volt.

At 0°.0 C.

No. I.		No. II.		No. III.	
Date	E.M.F. in Volt.	Date	E.M.F. in Volt.	Date	E.M.F. in Volt.
$^2/_6{}^{oo}$ 1h.50 p.m.	0.05571	$^2/_6{}^{oo}$ 1h.50 p.m.	0.05520	$^5/_6{}^{oo}$ 4h 50 p.m.	0.05571
2 25	0.05571	2 25	0.05408	5 24	0.05581
2 50	0.05571	2 50	0.05347		
$^4/_6{}^{oo}$ 11 15 p.m.	0.05591	$^4/_6{}^{oo}$ 11 15 p.m.	0.05082		
11 50	0.05591	11 50 p.m.	0.05092		
average	0.05579 Volt.			average	0.05576 Volt.

As regards this table it must be observed that the cells I and II were kept in ice from $^2/_6{}^{oo}$ to $^4/_6{}^{oo}$. They were then measured at $^4/_6{}^{oo}$, first at 0°,0 and then at 25°,0 C.

The result of these measurements is therefore, that whilst I, II and III have exactly the same E.M.F. at 25°,0 C. namely

I. = 0,04997 Volt.

II. = 0,04992 Volt.

III. = 0,04989 Volt.

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an important difference exists at 0°,0 C. between I and III on the one hand and II on the other.

I. = 0,05579 Volt.

II. = 0,05092 Volt.

III. = 0,05576 Volt.

It is moreover of importance to point out that I and III after they were cooled from 25°,0 C. to 0°,0 C. very soon reached their end-value whilst with II this was only the case after a few days.

5. The observations described immediately gave rise to the suspicion that the Cd-amalgam used in the cell is a metastable substance [1]). This, it is true, appeared to be in contradiction with the investigation of JÄGER [2]) who states that amalgams with 5—15 pCt. of Cd are unchangeable to $^1/_{100}$ millivolt but there were so many indications which appeared to contradict this, that I continued the investigation in the original direction. In what follows it will be seen that JÄGER's view is incorrect; the reason why he was unable to prove the instability of the 14.3 pCt. cadmium amalgam used will also appear.

6. I tried in the first place to find the temperature at which the difference between the cells I (and III) and II first appears.

For this purpose the E.M.F. of I and II was determined at different temperatures between 0°,0 C. and 25°,0 C.

The temperatures 5°, 10°, 15° and 20° were kept constant for a long time by allowing ice-water to flow from an elevated reservoir into a bath provided with stirring apparatus and toluene regulator, the supply being regulated by means of a tap. The heat given off by the flame is compensated for by the refrigeration caused by the iced water and in this manner the temperature may be kept constant all day long within 0°,03 C.

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[1]) It might be thought that metallic cadmium, which formed the negative electrode of the cells, might be metastable like tin. A special investigation, however, gave indications that such is *not* the case and I, therefore, occupied myself in the first place with the cadmium amalgam.

[2]) WIEDEMANN, Annalen 65, 107 (1898).

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TABLE IV.

Cell I.			Cell II.		
Temperature.	Time.	E.M.F. in Volt.	Temperature.	Time.	E.M.F. in Volt.
0°0	9h.	0.0559 [1])	0°0	9h.10	0.0509
	10 30	0 0559		10 40	0.0509
5°0	11 7	0.0549	5°0	11 12	0.0515
	11 30	0.0549		11 35	0.0515
10°0	12 0	0.0536	10°0	12 10	0.0517
	12 17	0.0536		12 22	0.0517
15°0	12 47	0.0524	15°0	12 52	0.0517
	2 20	0.0524		2 30	0.0517
20°0	3 10	0.0513	20°0	3 15	0.0510
	3 45	0.0513		3 50	0.0510
25°0	5 15	0.0501 [1])	25°0	5 20	0.0501 [1])
	5 50	0.0501		6 0	0.0501

If with these data we construct a curve which has the temperatures as abscissae and the electromotive forces as ordinates fig. 2 is obtained.

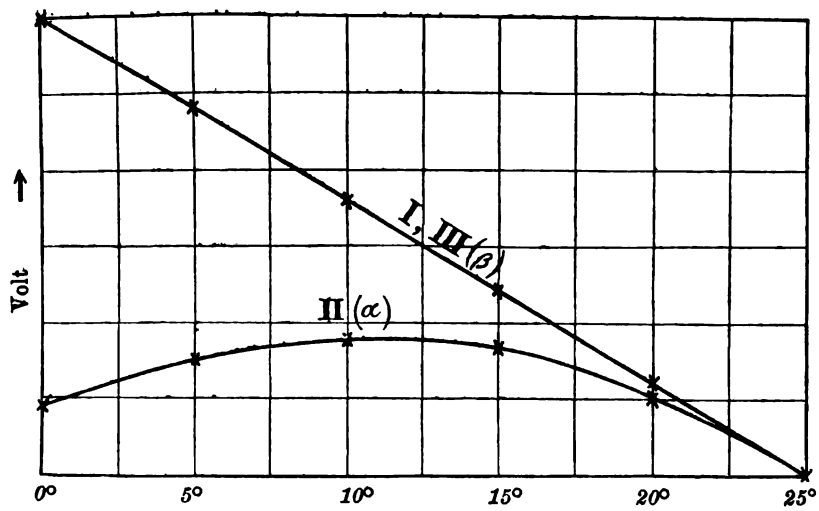

Fig. 2

The two curves intersect at about 23°.

From this it is seen that the cadmium amalgam (14.3 pCt. of Cd.) *contained in cell I and III is metastable below* 23°.

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[1]) These measurements took place 6 days after the cell had been constructed. It will be seen that in that time the E.M.F. has been raised about 0,0002 Volts. This corresponds with the observations of Richard and Lewis, Zeitschr. für phys. Chemie 28, 1. (1899) on Cd-electrodes of this kind.

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7. As these observations as we will see later on, are of great importance when judging of the suitability or otherwise of the WESTON-cells as standards, I have convinced myself of the correctness of these conclusions by the dilatometric process.

For this purpose the cadmium-amalgam which had served for the construction of the electrodes was introduced into a dilatometer filled with petroleum as measuring liquid.

That the amalgam is not in equilibrium at 0° is seen from the following observations:

TABLE V.

Time in hours.	Height of the level in the dilatometer.
0	107
2½	99
4	96
4¾	94
5¾	92
6¾	91
24	71
48	55
72	40

8. It now becomes more plain from the electric measurements (fig. 2) why JÄGER [1]), who according to his communication, made his measurements at about 20°, did not notice the metastability, for that temperature is so close to 23° that under these circumstances any change in the amalgam could only be observed after the lapse of an exceedingly long time.

9. Apparently the amalgam electrodes of the cells I (and III) and II had been treated in the same manner and yet that of II had changed into the stable modification whilst I and III continually remained metastable. That the change may often occur is

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[1]) See my previous communication p. 213.

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shown by the fact that of the three cells which I had made, one contained stable cadmiumamalgam [1]).

Provisionally we will call the amalgam contained in the cells I and III (the metastable modification below 23°) the β-amalgam whilst that in cell II will be given the name of α-amalgam.

From table IV we see that cells with the β-amalgam have at 0° an E. M. F. which is not less than 5 millivolt larger than those of the cells in which the α-amalgam forms the positive electrode.

10. The question now at once arises: Do the observations made by JÄGER and WACHSMUTH with the WESTON-cell relate to cells in which stable amalgam is present, or have they been made with cells which have the metastable body as negative electrode?

The fact that with some cells at 0° they found a higher E. M. F. than with others would indicate that they have mostly worked with the metastable modification This cannot, however, be stated with certainty, because it follows from the results of our investigation on the behaviour of cadmium sulphate that the presence of the stable form of this salt may have increased the E.M.F. at 0°.

I, therefore, have studied this point more closely. For this purpose the cells I, II and III were transformed into WESTON-cells (cells I^a, II^a and III^a) except that they were filled with a *clear* solution of $CdSO_4 . {}^8/_3 H_2O$ (stable modification) at 0° *without* any crystals at the bottom.

The dilute solution of $CdSO_4$ was poured out of *ABC* (previous communication fig. 1), the arm *A* provided with a layer of cotton-wool, and the metallic Cd removed from *C* and replaced by mercurous sulphate.

The solution of $CdSO_4 . {}^8/_3 H_2O$ (stable modification) saturated at 0° was prepared by mixing the anhydrous salt with water at 0°, care being taken to cool the liquid so as to prevent the temperature from rising over 15°.

The bottles containing the salt and the water were shaken for 4 hours at 0°.0 C. and the solution was filtered. The saturated solution thus obtained was introduced into I, II and III and the cells which previously had been rinsed with this solution were closed and brought, in the thermostat, to 0° C. The E.M.F. of the cells (I^a, II^a, III^a) was then determined.

In this way the following values were found:

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[1]) Compare BARNES l. c.

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TABLE VI.

		Temperature 0°.0 C.
WESTON-Cell	I*a*	1.0198 Volt.
WESTON-Cell	II*a*	1.0231 Volt [1])
WESTON-Cell	III*a*	1.0197 Volt.

We, therefore, see that all the measurements of JÄGER and WACHSMUTH have been made with WESTON cells which are *metastable*[2]).

11. The formula given by the Reichsanstalt for the connection between the E.M.F. of WESTON-cells and the temperature and which should be used between 5° and 26° C., therefore loses its value on account of these facts and, considering the metastability of the cadmium amalgam, is only true for temperatures between 23° C. and 26° C., whilst the metastability of cadmium sulphate as we have previously demonstrated is a second reason of its insuitability.

12. Since 1892, a standard-cell has been sold by WESTON at Newark (obtainable in Europe from the "European WESTON Electrical Instrument Co.", Berlin) which is constructed in accordance with the scheme:

Cd-amalgam 14.3 pCt. — solution of cadmium sulphate — Hg_2SO_4—Hg.
(Saturated at + 4° C.) without solid phase.

It was thought, even after our investigation on the change which $CdSO_4 . {}^8/_3 H_2O$ undergoes at 15° C., that this cell constituted a perfectly trustworthy standard, since above 4° C., no solid phase is present.

But since it has been proved that cadmium amalgam below 23° C. may occur in two modifications, it follows that even this standard may show a different E.M.F. below that temperature according to which of the two modifications of the amalgam is present.

13. Owing to the fact that both in the WESTON-cell of the Reichsanstalt and in that of the WESTON Co. there exists cadmium amal-

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[1]) It will be noticed that whilst at 0°.0 C. the difference in E.M.F. of the cells I (or III) and II amounted to 5 millivolt, the WESTON-cells showed a difference of 3,4 millivolt at that temperature. I will afterwards return to this matter.

[2]) Between 0° C. and 23° C.

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gam which readily remains in the metastable form (it must be remembered that all the measurements of the R. A. have been made with metastable cells) and that this amalgam may spontaneously pass into its stable form which change is accompanied by a change in the E.M.F. (up to 5 millivolt at 0°)] we must come to the conclusion *that both forms* [1]) *are unsuitable as standards of electromotoric force.*

A cell which at the time of its construction is compared with another standard and found to possess the E.M.F. indicated by the Reichsanstalt at the given temperature, may subsequently come to have some totally different E.M.F.

What is required of a standard cell is that, when constructed in a definite way, its E.M.F. shall be positively defined at a stated temperature; it will be seen from the foregoing that the WESTON-cells do not by any means conform to this specification.

14. Above 23° C. all the WESTON-cells, as seen from the foregoing, possess a sharply defined E.M.F. which follows the temperature formula given by the Reichsanstalt (to 26°). Only by making use of a thermostat in which the cell is placed when in use (and for some times beforehand in order to convert any metastable amalgam into the stable form) can these drawbacks be avoided. But then the great advantages which this standard seemed to possess compared with others with a larger temperature coefficient are lost. Moreover, working with thermostats is far too tedious for technical purposes.

15. After reading the above, the question naturally arises; do such complications arise with the CLARK-cell?

The amalgam which is used there as negative electrode has the composition $Zn : Hg = 1 : 9$.

Although my investigations in this direction are not yet quite finished, I think that it is very probable that we shall meet with similar phenomena. I mention, therefore, briefly the investigations of WILLOWS [2]) on the changes in the electrical conductivity of different amalgams at a constant temperature, when those amalgams have been exposed to changes in temperature.

For the sake of brevity I will here bring forward only one case

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[1]) The first named is moreover often metastable owing to the presence of the solid salt $CdSO_4 . {}^8/_3 H_2O$.

[2]) Philos. Magazine, November 1899, 433.

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from the large number studied by WILLOWS and choosé as an example, the zinc amalgam containing 9,5 pCt. of zinc and having therefore, about the same composition as the amalgam used in the CLARK-cells.

In fig. 3 the resistance of the amalgam as a function of the

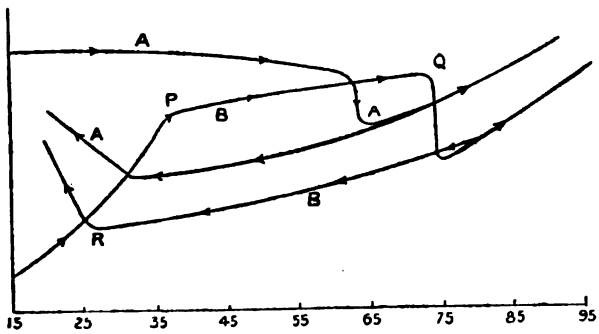

Fig. 3.

temperature is shown. The arrows indicate whether the temperature was rising or falling. The curve *A* was obtained immediately after the amalgam had been heated several times, whilst *B* represents the results which were found after the amalgam had been kept for some weeks at the temperature of the room.

It is plainly visible from this figure that the amalgam can have very different resistances at the same temperature, a good proof that even after a long time a condition of equilibrium in the amalgam is not reached.

WILLOWS has found similar curves for cadmium amalgam, but the amalgam which interests us here most (1 : 6) has not been investigated by him.

The former observations on cadmium sulphate and also those which have been communicated in this paper on cadmium amalgam may be summarised as follows:

Results of the Investigation.

1. Cadmium sulphate ($CdSO_4 . {}^8/_3 H_2O$) can exist below 15° C. in two modifications.

2. Cadmium amalgam (14.3 pCt. of Cd) can appear in two modifications [1]) below 23° C.

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[1]) The word "modifications" is here only preliminary. A further investigation will have to show what changes take place in the amalgam.

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3. At 0° C. a potential difference of 5 millivolt exists between those modifications of the cadmium amalgam.

4. *The* WESTON-*Cadmium-cells, both the form studied and recommended by the Physikalisch-technische Reichsanstalt, and that sold by the European Weston Electrical Instrument Co. are metastable systems* (below 23°) *which may pass quite spontaneously into the stable condition. As this change is coupled with a great change in the E.M.F. these cells are unsuitable for standard of electromotive force.*

5. The researches at the Reichsanstalt are made with *metastable* WESTON-cells and the temperature-formula given by JÄGER and WACHSMUTH therefore relates to *metastable* cells.

When a better insight into the behaviour of cadmium amalgams has been obtained a proposal may, perhaps, be made for the construction of a standard-cell which possesses all the advantages and none of the drawbacks of the WESTON-cell.

Mr. H. C. BIJL has already made a beginning with the investigation of these amalgams in this laboratory.

Amsterdam, University Chem. Lab., June 1900.

(August 28, 1900.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN

TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 29, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 September 1900 Dl. IX).

CONTENTS: "Contributions to the knowledge of some undescribed or imperfectly known fungi" (2nd Part). By Prof. C. A. J. A. OUDEMANS, p. 230. — "On the origin of new species of plants". By Prof. HUGO DE VRIES, p. 245. — "On muscle-tone" (abstract). By Dr. J. W. LANGELAAN (Communicated by Prof. T. PLACE), p. 248. — "On the determination of sensory spinal skinfields in healthy individuals". By Dr. J. W. LANGELAAN (Communicated by Prof. C. WINKLER), p. 251 (with one plate). — "Curious disturbances of the sensation of pain in a case of tabes dorsalis". By D. H. BEIJERMAN (Communicated by Prof. C. WINKLER), p. 253 (with one plate). — "The so-called opake minerals in transmitted light". By Prof. J. L. C. SCHROEDER VAN DER KOLK, p. 254. — "On the spacial anharmonic ratio of curves ρ^n of order n in the space S_n with n dimensions". By Prof. P. H. SCHOUTE, p. 255. — "Preservatives on the stigma against the germination of foreign Pollen". By Dr. W. BURCK (Communicated by Prof. HUGO DE VRIES), p. 264. — "Contributions to the knowledge of VAN DER WAALS' ψ-surface. I. Graphical treatment of the transverse-plait". By Prof. H. KAMERLINGH ONNES, p. 275 (with 2 plates). — "Contributions to the knowledge of VAN DER WAALS' ψ-surface. II. The part of the transverse-plait in the neighbourhood of the plaitpoint in KUENEN's experiments on retrograde condensation". By Prof. H. KAMERLINGH ONNES and Dr. M. REINGANUM, p. 289 (with 2 plates). — "On the measurement of very low temperatures. III. Coefficient of pressure variation of pure hydrogen between 0° and 100°". By Prof. H. KAMERLINGH ONNES and M. BOUDIN, p. 299 (with one plate). — "On the HALL-effect and the resistance of crystals of bismuth within and without the magnetic field". By Dr. E. VAN EVERDINGEN JR. (Communicated by Prof. H. KAMERLINGH ONNES), p. 316. —

The following papers were read:

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Botanics. — "*Contributions to the knowledge of some undescribed or imperfectly known Fungi*" (2nd Part) [1]). By Prof. C. A. J. A. OUDEMANS.

II. FUNGI SECUNDARII sive INFERIORES.

† SPHAEROPSIDEAE.

a. Sphaeroideae.

α. Hyalosporae.

PHYLLOSTICTA Persoon.

6. PHYLLOSTICTA AESCULANA Oud. n. sp. On the leaves of *Aesculus Hippocastanum*. Nunspeet, Oct. 2, 1899; Mr. BEINS.

Perithecia primo sub epidermide occultata, postea exposita, sparsa, subglobosa, nigra; sporulae ellipticae, hyalinae, ad polos late rotundatae, nitide biocellatae, 6—7 × $3^1/_2$—$4^2/_3$ μ. Differt ab omnibus affinibus (*Phyll. aesculina* Sacc., *Phyll. sphaeropsidea* Ell. et Ev., *Phyll. Aesculi* Ell. et Mart. et *Phoma aesculina* Sacc.) dimensione sporularum majore vel minore, seu mutata ratione longitudinem sporularum inter et latitudinem (Pl. IV, fig. 2).

7. PHYLLOSTICTA ALNEA. Oud. n. sp. On the leaves of *Alnus glutinosa*. Nunspeet, Oct. 13, 1899; Mr. BEINS. — Maculae amphigenae, utrimque fertiles, 2—10 mill. in diam., pallide ferrugineae, tandem a partibus sanis viridibus vicinis descissentes. Perithecia minima, fuliginea, sphaerica, prominentia. Sporulae hyalinae, rectae vel subcurvatae, $4^1/_3$ — 7×$2^1/_3$ μ. — Differt a *Phyll. alnicola* Cooke et Massee (Contrib. Mycol. Vér. 18; Sacc., Syll. IX, 117) sporulis manifeste majoribus ($4^2/_3$—7 × $2^1/_3$ μ contra 2.38×0.7 μ).

8. PHYLLOSTICTA BRACTEARUM Oud. n. sp. — On the bracts of the female inflorescences of *Humulus Lupulus*. — Nunspeet, 8 Dec. 1898; Mr. BEINS. — Maculae nullae. Perithecia sparsa, nigra, coriacea, $^1/_{10}$—$^1/_6$ mill. in diam., poro apicali destituta. Sporulae bacillares, rectae, hyalinae, eguttulatae, parvae (4—$4^2/_3$×$1^1/_2\mu$), ad polos rotundatae.

When applying stronger lenses it appears that in both poles a small, drop-shaped body is hidden.

9. PHYLLOSTICTA BUFONII Oud. n. sp. (Phoma Bufonii Oud. in

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[1]) For 1st Part see these Proceedings p. 140.

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Hedw. XXXVI, (1898) p. 313). On the leaves of *Juncus bufonius.* — Nunspeet, March 1898; Mr. BEINS. — Perithecia sparsa, primo tecta, postremo exposita, $^1/_8$—$^1/_6$ mill. in diam., nigerrima, membranacea, centro poro pertusa; sporulae achromae, continuae, ellipticae, eguttulatae, 9×4 μ.

10. PHYLLOSTICTA FAGI Oud. n. sp. — On the leaves of *Fagus silvatica.* — Nunspeet, Oct. 30, 1899; Mr. BEINS. — Maculae amphigenae, fertiles tantum in pagina superiore, dilutissime fuligineae, $^1/_2$ circa cent. in diam., sed saepe confluentes. Perithecia epiphylla, maculicola, exilissima, $^1/_{12}$—$^1/_{10}$ mill. in diam., dense distributa, orbicularia, opaca. Sporulae minutisimae, bacillares, $4^2/_3 \times 1^1/_6$ μ, immixtis paucis 7 μ., hyalinae, continuae, guttulis expertes, ad polos rotundatae, basidiis filiformibus longiusculis suffultae.

11. PHYLLOSTICTA HOLOSTEICOLA Oud. n. sp. — On the leaves of *Stellaria Holostea.* — Nunspeet, April 17, 1900; Mr. BEINS. — Perithecia amphigena, vulgo autem epigena, in maculis pallide griseis foliorum siccatorum subprominentia, vulgo numerosa et conferta, submicantia, $^1/_8$—$^1/_6$ mill. in diam., tenera, subfuliginosa. Sporulae cylindricae, rectae vel subcurvatae, ad polos late-rotundatae, 16—$20 \times 4^2/_3$—$5^1/_2$ μ, biocellatae, guttulis, volumine sporularum in rationem inducto, pusillis.

12. PHYLLOSTICTA ILICIS Oud. n. sp. — On the leaves of *Ilex Aquifolium.* — Nunspeet, May 28, 1899; Mr. BEINS. — Maculae valde extensae, ad ambitum multo pallidiores, irregulariter limitatae, hypogenae. Perithecia hypogena, rarissime epigena, gregaria, atra, micantia, prominula, primo occultata, postea exposita, centro perforata, $^1/_8$—$^1/_4$ in diam. — Sporulae ellipticae vel breviter-oblongae, utrimque rotundatae, hyalinae, protoplasmate aequali repletae, 5—7×2—3 μ.

13. PHYLLOSTICTA LABURNI Oud. n. sp. — On the leaves of *Cytisus Laburnum.* — Nunspeet, Oct. 25, 1899; Mr. BEINS. — Maculis arescendo albidae, diversiformes, 1—$1^1/_2$ cent. in diam., non marginatae; perithecia irregulariter distributa, atra, semiglobosodepressa, opaca, $^1/_6$—$^1/_4$ mill. in diam., tandem poro pertusa; sporulae hyalinae, oblongae vel ovato-oblongae, ad polos rotundatae, 9—12×3 μ, biguttatae, guttulis majoribus saepe minoribus paucis concomitatis. — Differt a *Ph. laburnicola* Sacc. Mich. I, 152 et Syll. III, 10, macularum praesentia, et peritheciis sporulisque majoribus (166—250 contra 60—70 μ, et 9—12×3 contra 3—5×1 μ).

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14. PHYLLOSTICTA NARCISSI Oud. n. sp. — On the leaves of a cultivated species of *Narcissus*. — Noordwijk, June 18, 1898. — In company of *Heterospora gracilis* and *Septoria Narcissi*. — Perithecia amphigena, numerosissima, conferta, tamen inaequaliter distributa, innata, 40 μ in diam., membrana valde subtili praedita; cirrhi, ubi adsunt, sphaerici, dilutissime rosei. Sporulae ellipticae aut oblongae, rectae vel curvatae, hyalinae, continuae, biocellatae, $4^2/_3$—$14 \times 2^1/_3$—$3^1/_2$ μ, guttulis valde distinctis.

*PHYLLOSTICTA PERSICICOLA Oud. n. sp. — On the blown-up portions of Peach-leaves attacked by Exoascus deformans. — Apeldoorn, June 1898; O. — Hedw. XXXVII (1898) p. 313.

15. PHYLLOSTICTA PODAGRARIAE Oud. n. sp. — On the leaves of *Aegopodium Podagraria*, in company of *Discosia Artocreas* and *Septoria Podagrariae*. — Nunspeet, Oct. 14, 1899; Mr. BEINS. — Maculae amphigenae, pallide ferrugineae, valde extensae, irregulariter limitatae, utrimque fertiles. Perithecia sparsa, sub epidermide occultata, $^1/_{12}$—$^1/_{10}$ mill. in diam., fuliginosa, depressa, tandem centro perforata. Sporulae ellipticae vel ovatae, ad polos rotundatae, continuae, hyalinae, guttula nitida in quovis polo praeditae, 7—$7.2 \times 2^1/_3$—$4^2/_3$ μ. — Species nostra toto coelo differt a *Phoma Podagrariae* West. (Not. III, Bull. Acad. r. de Belg. XIX, 1852, p. 116 et Sacc. Syll. III, 169) cujus synonyma sunt: *Sphaeria Podagrariae* Roth, *Dothidea Podagrariae* Fr. et *Septoria Podagrariae* Lasch.

*PHYLLOSTICTA QUERCICOLA Oud. n. sp. — At the under face of the leaves of *Quercus Robur*. cf. Hedw. XXXVII (1898) p. 175.

16. PHYLLOSTICTA TRAPPENII Oud. n. sp. — On the leaves of *Fraxinus juglandifolia*. — Naaldwijk 1864; the late Dr. J. E. VAN DER TRAPPEN. — Maculae amphigenae, vulgo valde extensae (ad 3 dec. in diam.), obscure limitatae. Perithecia nigra, numerosa, aequaliter distributa, adulta $^1/_6$ mill. in diam., prominentia. Sporulae oblongae vel elongato-ellipticae, ad polos rotundatae, hyalinae, $7 \times 2^1/_3$ μ.

17. PHYLLOSTICTA VINCICOLA Oud. n. sp. — On the leaves of *Vinca major*. Nunspeet, July 9, 1899; Mr. BEINS. — Maculae amphigenae, nigrae, quoad formam et dimensiones valde diversae, irregulariter limitatae, utrimque fertiles. Perithecia minima, in parenchymate foliorum abscondita, vertice perforata. Sporulae initio in

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globulum albidum, perithecii orificium obstruentem coalitae, singulae ellipticae, ad polos obtusissimae, hyalinae, biocellatae, basidiis filiformibus, sporulis multo longioribus suffultae, $3^1/_2—4^2/_3 \times 1^3/_4—2\mu$. — Differt a *Phyll. Vincae* Thüm., *Phyll. Vincae majoris* Allescher, *Macrophoma Vincae* Berl. et Vogl. et *Macrophoma cylindrospora* Berl. et Vogl., nunc praesentia guttularum, tunc iterum dimensionibus sporularum reductis.

PHOMA Fries.

18. PHOMA AMYGDALI Oud. n. sp. — On the leaves of *Amygdalus communis*. Nunspeet, April 27, 1899; Mr. BEINS. — Perithecia parva ($^1/_{10}$ mill.), centro perforata. Sporulae breve-ellipticae, $4—5 \times 3\ \mu$, hyalinae, continuae, guttulis destitutae.

19. PHOMA COLCHICAE Oud. n. sp. — On the petioles of *Staphylea colchica*. — Nunspect, March 1898; Mr. BEINS.

Perithecia numerosa, $^1/_4—^1/_2$ mill. in diam., per totam petiolorum superficiem irregulariter dispersa, epidermide perpetuo tecta, prominentia, vertice exposito perforata, circa ostiolum epidermidis portiuncula annulari nigrefacta ornata. Sporulae angustius vel latius oblongae, rectae, perfecte hyalinae, ad polos obtusiusculae, continuae, nitide 2-, 3-vel 4-guttalatae, $8—10 \times 3—4\ \mu$.

Maculae stromaticae nigrescentes, linea atra subinde distinctissime cinctae, quarum mentio facta est a mycologis Berlese et Voglino in descriptione *Phomae Brunaudi* (Sacc. Syll. III, 150), in ramulis nostris certe non defecerunt; relationem attamen has inter et perithecia supra descripta revera existere, nobis non licuit.

Phoma colchicae ab affinibus *Ph. Robergeana*, *Ph. Staphyleae* et *Ph. Brunaudi*, omnibus ramorum *Staphyleae colchicae* incolis, luculenter differt guttularum valde conspicuarum, nitidissimarum in sporulis praesentia, nec non peritheciorum volumine.

20. PHOMA CORNICOLA Oud. n. sp. — On the branches of *Cornus alba*. — Naaldwijk, 1866; the late Dr. J. E. VAN DER TRAPPEN.

Maculae nullae. Perithecia numerosissima, conferta, perpetuo sub epidermide occultata, prominentia, vertice exposito perforata, $^1/_4$ mill. in diam. Sporulae ellipticae, $5 \times 2^1/_2\ \mu$, rectae, hyalinae, continuae, biocellatae.

Differt nostra species a *Phoma Corni* sporulis suis minoribus ($5 \times 2^1/_2\ \mu$ contra $8—10 \times 2—3\ \mu$), rectis, ellipticis (neutiquam oblongo-cylindricis); a *Phoma thallina* absentia macularum linea purpurina limitatarum; a *Phoma Corni suecicae* peritheciis confertis, nec non

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sporulis suis ellipticis (neque cylindricis); a *Phoma candidula* perithecis confertis, nec non sporulis suis ellipticis, rectis (nec cylindricis, rectis et curvatis commixtis).

* PHOMA DESCISCENS Oud. n. sp. — On branchlets of *Vitis vinifera*. cf. Hedwigia XXXVII (1898) p. 314.

* PHOMA DOUGLASII Oud. n. sp. — On the cone-scales of *Abies Douglasii*. cf. Hedwigia XXXVII (1898) p. 314.

21. PHOMA COSMI Oud n. sp. — On the stems of *Cosmus bipinnatus*. — Nunspeet, Sept. 5, 1899; Mr. BEINS.

Perithecia caespitosa, nigra, globuloso-depressa, sub epidermide abscondita, $^1/_{10}$—$^1/_6$ mill. in diam., minute papillata, vertice perforata; sporulae oblongae, continuae, hyalinae, ad polos rotundatae, eguttulatae, $9^1/_3 \times 2^1/_2\ \mu$.

22. PHOMA EUPHORBIPHILA Oud. n. sp. — On the stems of *Euphorbia Lathyris*. — Naaldwijk, Dec. 1866; the late Dr. J. E. VAN DER TRAPPEN.

Perithecia numerosissima, conferta totamque internodiorum superficiem occupantia, perpetuo sub epidermide occultata, parum prominentia, tandem vertice exposito perforata et circa ostiolum portiuncula epidermidis annulari nigricante ornata, $^1/_4$ mill. sine, mill. 1 cum zona nigricante in diam. metientia. Sporulae oblongae vel subclavatae, rectae vel curvatae, 7—$9 \times 2^1/_2\ \mu$, 1- ad 4-guttulatae, hyalinae, continuae.

*PHOMA FRANGULAE Oud. n. sp. — On thin branches of *Rhamnus Frangula*. cf. Hedw. XXXIV (1898) p. 314.

23. PHOMA HAMAMELIDIS Oud. N. K. A. 3, I, 487. — This should be *Phoma Halesiae* Oud. n. sp. On branches of *Halesia tetraptera*. Nunspeet, March 7, 1898; Mr. BEINS.

The name of the plant was first given me wrongly, later correctly.

24. PHOMA IDAEI Oud. n. sp. — On the branches of *Rubus idaeus*. — Nunspeet, Febr. 3, 1899; Mr. BEINS.

Perithecia orbiculari-depressa, $^1/_5$—$^1/_4$ mill. in diam., vertice perforata, membrana justo crassiore praedita, perpetuo sub epidermidis portiunculo scutiformi, elliptico vel oblongo, nigro et paullo micante, ad polos acutato, 1—2×1 millim., occultata. Sporulae ellipticae vel oblongae, ad polos rotundatae, hyalinae, biocellatae, 7 — $8^1/_6 \times 2^1/_3$—$3^1/_2\ \mu$, basidiis sporularum longitudinem attingentibus suffultae.

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* PHOMA INEXPECTATA Oud. n. sp. — On the leaves of *Abies pectinata*. Cf. Hedw. XXXVII (1898), p. 176.

* PHOMA INOPINATA Oud. n. sp. — On the leaves of *Pinus Strobus*. Cf. Hedw. XXXVII (1898), p. 177.

25. PHOMA LARICIS Oud. n. sp. — On the twigs of *Larix decidua*. Scheveningen, May 1894.

Perithecia caespitose aggregata, subglobosa, primo sub peridermate abscondita, postea exposita, atra, 100—250 μ in diametro. Sporulae ellipticae, hyalinae, continuae, eguttalatae, $7 \times 2^1/_2$ μ.

26. PHOMA NEGUNDINIS Oud. n. sp. — On the branches of *Negundo fraxinifolia*.

Perithecia numerosissima, primitus sub peridermate abscondita, tandem exposita, 140 μ in diam., ochracea, vertice perforata. Sporulae ellipticae, continuae, hyalinae, $4^2/_3 \times 3^1/_2$ μ.

27. PHOMA OENOTHERICOLA Oud. n. sp. — On the leaves of *Oenothera biennis*. Nunspeet, March 13, 1898; Mr. BEINS.

Perithecia inordinate distributa, sub epidermate latentia, lentiformia, vertice perforata, $^1/_{10}$ mill. in diam. Cellulae epidermales ostiolo perithecii contiguae saturatius tinctae quam aliae magis distantes. Sporulae breviter oblongae, $7 \times 2^1/_2$ μ, eguttulatae, hyalinae.

Differt haec nostra species a *Phoma oenotherella* Sacc. sporulis angustioribus ($7 \times 2^1/_2$ μ contra 7×4 μ) et colore cellularum perithecii ostiolum circumdantium; a *Phoma Oenotherae* Sacc. et *Phoma Onagrarearum* Cooke guttularum in sporulis absentia; a *Phoma Onograrearum* insuper sporularum latitudine minore ($7 \times 2^1/_2$ μ contra $6—8 \times 3^1/_2—4$ μ).

*PHOMA QUERNEA Oud. n. sp. On branches of *Quercus Robur*. — Nunspeet, March 7, 1898; Mr. BEINS. Cf. Ned. Kr. Arch. 3, I, 489.

28. PHOMA SACCARDOI Oud. — On branches without bark of *Sambucus nigra*. Naaldwijk, 1864; the late Dr. J. E. VAN DER TRAPPEN.

When on p. 491 of the 1st volume of the 3rd series of the "Nederlandsch Kruidkundig Archief" (1898) I mentioned *Phoma vicina* Desm. as a new indigena for our country, I pronounced the supposition that *my* specimens would not differ from those described by Mr. SACCARDO in Syll. III, 71, notwithstanding the measurements (5×2 μ) of the spores examined by the Italian mycologist, did not correspond with those of DESMAZIÈRES and of myself ($7—5 \times 1.9$ μ). At that time I had not however, had an opportunity of getting acquainted with *Phoma vicina* Saccardo, which is bound to branches

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deprived of bark of *Sambucus nigra*. Now, however, that I have come into possession of such objects, I have been enabled to convince myself that such an identity between both Phomas, as to which I referred above, does not exist, and that consequently, they cannot be indicated by one and the same name. For this reason I supplied *Phoma vicina* Sacc. by *Phoma Saccardoi*.

To be sure, it cannot be denied that in both species the base of the perithecia dives down to a slight depth into the wood of the branches, but this does not prevent the perithecia of *Phoma vicina* Desm. from having a much more robust appearance, and thicker walls, and from its never occurring but on the branches of the elder covered with bark, whilst those of *Phoma Saccardoi* Oud. are much more delicate and small, have a transparent membranaceous wall, and prefer branches devoid of bark.

*PHOMA SALICELLA Oud. n. sp. — On the branches of *Salix cinerea*. — Nunspeet, March 7, 1898; Mr. BEINS. — Cf. N. Kr. Arch. 3, I, p. 490.

29. PHOMA SALISBURYAE Oud. n. sp. — On the branches of *Salisburya adianthifolia*. — Botanical Garden Leiden, Aug. 1893.

Perithecia numerosa, inordinate distributa, orbicularia, nigra, $^1/_4$—$^1/_3$ mill. in diam., primo sub peridermate latentia, postea in fissuris corticis exposita, vertice perforata. Sporulae fusiformes, ad polos anguste rotundatae, hyalinae, continae, eguttulatae, 9×2 μ.

*PHOMA SEMPERVIRENTIS Oud. n. sp. — On the still green branches of *Lonicera sempervirens*. — Nunspeet, April 15, 1898; Mr. BEINS. — Cf. Hedw. XXXVI (1898) p. 315.

30. PHOMA SOLANIPHILA Oud. n. sp. — On the stems of *Solanum nigrum*. — Nunspeet, Dec. 19, 1899; Mr. BEINS.

Perithecia laxe caespitosa, sub epidermide latentia, postremo exposita, sphaeroideo-depressa, 140—160 μ in diam., nigra, vertice perforata. Sporulae ellipticae, hyalinae, continuae, eguttulatae, ad polos rotundatae, $4^2/_3$—$7 \times 2^2/_3$—3 μ.

Differt a *S. dulcamarina*, *pampeana*, *Dulcamarae* et *solanicola*, absentia guttularum, et a *P. europaea* et *Solani* sporularum dimensionibus desciscentibus.

*PHOMA SUBTILISSIMA Oud. n. sp. — On the dried peduncles of *Cytisus Laburnum*. — Cf. Hedw. XXXVII (1898) p. 315.

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31. PHOMA TATARICOLAE Oud. n. sp. — On the branches of *Lonicera tatarica* not yet deprived of their bark. — Nunspeet, March 5, 1899.

Perithecia numerossima, nunc totam internodiorum superficiem occupantia, tunc vero gregatim conferta limitesque macularum pallescentium valde extensarum non excedentia, sub peridermate occultata, postea autem vertice suo perforato, intra zonulam nigrescentem incluso, exposita. Sporulae nunc ellipticae, tunc vero paullo elongatae, ad polos rotundatae, biocellatae, hyalinae, $7—8 \times 3^1/_2—4$ μ.

Species neutiquam confundenda neque cum *Ph. oblongata* Briard et Henrich (Sacc. Syll. X, 145), nec cum *Ph. Mariae*, quae ambae *lignicolae*; neque cum *Ph. cryptica* Sacc. (Syll. III, 69), cujus sporulae forma recedunt; neque cum *Ph. minutula* Sacc. (Syll. III, 70), cujus sporulae voluminosiores; neque cum *Ph. tatarica* Allescher (Wint. Kr. Fl. VI, 221), cujus sporulae non tantum voluminosiores sed insuper forma recedunt; neque cum *Ph. xylostei* Cooke et Harkness (Sacc. Syll. III, 70) et *Ph. viventis* Cooke (Sacc. Syll. X, 145), quarum sporulae voluminosiores.

32. PHOMA THYRSIFLORAE Oud. n. sp. — On the stems of *Lysimachia thyrsiflora*, in company with *Ascochyta Lysimachiae* Oud. Nunspeet, April 15, 1898; Mr. BEINS. — Maculae nullae. Perithecia minima ($^1/_{10}$ mill. in diam.), laxe caespitosa, sub peridermate occultata, prominentia, denique vertice perforata. Sporulae breve-ellipticae, hyalinae, eguttulatae, $3^1/_2—5 \times 2^1/_3—3$ μ.

Differt a *Ph. Lysimachiae* sporulis multo minoribus ($3^1/_2—5 \times 2^1/_3—3$ μ contra $10 \times 4^1/_2—5$ μ).

33. PHOMA TRIACANTHI Oud. n. sp. — On the thorns of *Gleditschia triacanthos*, in company with *Ph. Gleditschiae*. — Nunspeet, March 18, 1899; Mr. BEINS.

Perithecia nunc aequaliter distributa, tunc caespitose aggregata, majoribus et minoribus commixtis, sub peridermate latentia, p. m. prominentia, denique in fissuris longitudinalibus rectis vel curvatis, simplicibus vel ramosis, exposita. Sporulae oblongae, ad polos late rotundatae, hyalinae, nitidae biocellatae, $7 \times 2^1/_3$ μ.

34. PHOMA TYPHICOLA Oud. n. sp. — On the stems of *Typha latifolia*. — Nunspeet, May 21, 1899; Mr. BEINS.

Perithecia primo sub epidermide latentia, postremo exposita, minima, nigra. Sporulae ellipticae vel oblongae, ad polos rotundatae, continuae, hyalinae, eguttulatae, $3^1/_2—5 \times 2^1/_3$ μ. (Pl. IV, fig. 3).

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35. PHOMA VIBURNICOLA Oud. n. sp. — On the branches of *Viburnum Oxycoccos*, in company with *Ascochyta viburnicola*. — Nunspeet, April 14, 1899; Mr. BEINS.

Perithecia numerosa, parva, diu sub peridermate occultata. Sporulae ellipticae, hyalinae, continuae, eguttulatae, 5—6 × 3½ *u*.

MACROPHOMA Berlese et Voglino.

36. MACROPHOMA CAPSELLAE Oud. n. sp. — On the leaves of *Capsella Bursa pastoris*. — Apeldoorn, July 26, 1899; O. — Perithecia conferta, primo epidermide velata, denique exposita, nigra. Sporulae ellipticae vel elliptico-oblongae, hyalinae, continuae, ad polos rotundatae, biocellatae, 16 × 6 *μ*.

The size of the spores does not allow this species to be admitted into the genus *Phyllosticta*.

37. MACROPHOMA ILICIS (Desm.) Oud. — On the leaves of *Ilex Aquifolium*. Described by DESMAZIÈRES under the name of *Phoma Ilicis* in his „Plantes Cryptogames de France", 1e S., 1e Ed., N°. 1290, and taken up by SACCARDO under the same name in Syll. III, p. 106.

Perithecia hypophylla, numerosissima, subconferta, saepe intra limites macularum pallescentium coacervata, valde prominentia, sub epidermide occultata, vertice perforata, nigra, ⅕ ad ¼ mill. in diam. Sporulae ellipticae vel ovatae, hyalinae, continuae, 12—15 × 6—7 *μ*, initio protoplasmate nebuloso repletae, denique guttula voluminosa centrali ornatae, ad polos late rotundatae, longe pedicellatae, apice passim apiculatae.

Now that the genus *Macrophoma* has been introduced into science for those species of *Phoma*, whose spores are 15 or more mikrons in length, it was necessary to bring *Phoma Ilicis* Desm. under this head. With the name in SACCARDO's Syll. (III, 106) the same ought to be done.

SCLEROTIOPSIS Spegazzini.

38. SCLEROTIOPSIS POTENTILLAE. Oud. n. sp. — On the leaves of *Potentilla procumbens* (Tormentilla reptans). — Nunspeet, August 26, 1898; Mr. BEINS.

Perithecia innata, semiglobosa, nigra, submicantia, adulta p. m. 1 mill. in diam., nunc ad faciem foliorum superiorem, tunc vero ad inferiorem prominentia, absque ullo ostioli vestigio, membrana fragili, indistincte parenchymatosa instructa. Basidia filiformia, recta. Spo-

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rulae acrogenae, solitares, cylindricae, semilunares, indistincte mucronatae, hyalinae, continuae, $7-9^1/_3 \times 2\,\mu$. — (Pl. IV, fig. 4).

Our description of *Scl. Potentillae* corresponds almost entirely with that of *Scl. australasiaca*, made known by SPEGAZZINI in SACCARDO's Syll. III, p. 184. As, however, between the shape and the internal colour of the perithecia of both fungi, the size of their spores, and the nature of their host-plant, greater and smaller differences were to be observed, I thought myself justified in allowing both Scl.: *Scl. Potentillae* on *Potentilla procumbens* and *Scl. australasiaca* on *Eucalyptus Globulus*, to continue as two species and not to join them to one.

39. SCLEROTIOPSIS PITYOPHILA (Cda) Oud.; Phoma pithyophila Sacc. Syll. III, 101; Allescher in Wint. Kr. Fl. VI, 199; Sphaeronema pithyophila Corda Ic. Fg. 40 et tab. VIII, fig. 116. — On the leaves of *Pinus silvestris*. — Nunspeet, 1899; Mr. BEINS.

Perithecia amphigena, primo abscondita, in acuum parenchymate immersa, postremo exposita, corporaque sistentia sclerotiformia, nigra, nunc separata et subsphaerica, tunc vero coalita et irregularia. Quodvis corpusculum e stratis quasi duobus compositum: uno scil. magis superficiali, parenchymatoso, nigrescente, crassiore, densiore; altero, magis interiore, parenchymatoso, pallide-flavo, tenuiore, molliore, dum constat colorem nigrescentem cellularum membranis, colorem pallide-flavum vero cellularum contentis esse proprium. Sporulae maturae ex orificio accidentali, irregulari, non autem ex ostiolo naturali protrusae, corpuscula sistunt oblonga, hyalina, ad polos rotundata, uniguttulata (?)

RABENHORSTIA Fries.

*RABENHORSTIA CLANDESTINA Fr.; Sacc. Syll. III, 244. On dead branches of *Sorbus Aucuparia*. — Nunspeet, May 9, 1898; Mr. BEINS.

A detailed description of this hardly known fungus, which has only very superficiously been described by SACCARDO, I gave in Hedwigia XXXVII (1898) p. 315.

*RABENHORSTIA SALICIS Oud. n. sp. — On the branches of *Salix repens*. Nunspeet, May 5, 1898; Mr. BEINS. — Hedw. XXXVII (1898) p. 317.

PLACOSPHAERIA Saccardo.

40. PLACOSPHAERIA PRUNI Oud. n. sp. — On the young branches of *Prunus domestica*. Nunspeet, April 27, 1899; Mr. BEINS.

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Stromata ad ramulorum superficiem numerosa, oblonga, $^1/_2$ ad 1 centim. longa, 2 ad 3 mill. lata, juniora rufescentia, vetustiora fuliginea, intermixtis nonnullis annulo fuliginoso ad ambitum inclúsis, centroque rufescente, subprominente. Includunt cavernulas plures indivisas, basidiis filiformibus, conidia quoad longitudinem subaequantibus, vestitas. Conidia partim cylindrica, ad polos rotundata, partim fusiformia, subacutata, semper hyalina, 2-vel pluriocellata.

FUSICOCCUM Corda.

41. Fusicoccum Corni Oud. n. sp. — On the branches of *Cornus alba*. — Nunspeet, Sept. 15, 1899; Mr. Beins.

Perithecia vulgo maculicola, sparsa, nigra, sub peridermate abscondita, p. m. prominentia, $^1/_3$—$^1/_2$ mill. in diam., tandem vertice perforata, plurilocularia, loculis septisque membranaceis; sporulae fusiformes, ad polos anguste-rotundatae, 9 — 12 × 2—$3^1/_2$ μ, continuae, hyalinae, eguttulatae; basidia acicularia, sporis duplo longiora.

CYTOSPORELLA Sacc.

42. Cytosporella Quercus Oud. n. sp. — On branches of *Quercus Robur*. — Valkenburg (L.); April 1900; Mr. J. Rick.

Stromata corticola numerosa, sparsa, polymorpha, saepe sinuoso-limitata, verruciformi-depressa, 1 ad 3 cent. lata, intus fuscescentia, incomplete pluricellularia, locellis quoad amplitudinem valde variabilibus; sporulae globulosae, hyalinae, ad basin subcontractae, $9^1/_3$—$11^2/_3$ μ, basidiis brevibus suffultae.

Differt a *C. Populi* Oud. (Ned. Kr. Arch. 2, V, 494; Sacc. Syll. X, 242) stromatibus multo robustioribus et sporulis multo majoribus ($9^1/_3$—$11^2/_3$ μ contra 7 μ).

CYTOSPORA Ehrenberg.

43. Cytospora dasycarpi Oud. n. sp. — On the branches of *Acer dasycarpum*. — Scheveningen, May 1895; Bussum, April 1900; Mr. Koning.

Pustulae sparsae, quoad amplitudinem magnopere variabiles, convexae, primo clausae, postea, peridermate varie fisso, perviae. Stromata nigra, intus lacunosa, lacunis septis spuriis in loculamenta plurima inaequalia concentrice divisis. Sporulae fere globulosae, cum ellipticis et brevi-fusiformibus inaequaliter mixtae, continuae, hyalinae, 1—3 × 1—2 μ, basidiis longis, tenerrimis suffultae.

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44. CYTOSPORA FRAXINICOLA Oud. n. sp. — On the young, thin branches of *Fraxinus excelsior*. — the Hague, April 1889.

Differt a *C. Fraxini* Delacroix (Bull. de la Soc. mycol. de France, 1890, p. 184 et tab. XX fig. V; SACCARDO Syll. X, 245) basidiis multo longioribus (25 μ contra 10 μ) et sporulis angustioribus ($7 \times 1^1/_2\ \mu$ contra $7 \times 2^1/_2\ \mu$).

*CYTOSPORA OPACA Oud. n. sp. — On the branches of *Ilex opaca*. Cf. N. K. A. 3, I, 492 et Hedw. XXXVII (1898) p. 177.

*CYTOSPORA SELENESPORA Oud. n. sp. — On the branches of *Sorbus Aucuparia*. — Nunspeet, March 3, 1898; Mr. BEINS. — Cf. Ned. Kr. Arch. 3, I, 493.

CEUTHOSPORA Greville.

45. CEUTHOSPORA FRAXINICOLA Oud. n. sp. — On branches of *Fraxinus excelsior*. — Amsterdam, January 1877; O.

Stromata numerosa, inordinate distributa, primo occultata, tandem exposita laciniisque peridermatis rupti circumcincta. Perithecia caespitose aggregata, parte sua dimidia superiore rotundata libere prominentia, coriacea, nigra, sine ostioli vestigio. Sporulae minimae, bacillares, hyalinae, simul cum magna mucilaginis copia ex variis evolutionis centris protrusae, $4^1/_3 \times 1^1/_6\ \mu$, singulae basidio filiformi 9 μ p. m. longo suffultae.

Differt nostra a *C. Fraxini* Tognini (Seconda Contrib. micol. tosc. p. 10 et Sacc. Syll. IX, 510), cujus plena diagnosis adhuc desideratur, sporulis multo minoribus ($4^1/_3 \times 1^1/_6\ \mu$ contra $6—7 \times 3\ \mu$).

β. Phaeosporae.

CONIOTHYRIUM Corda.

46. CONIOTHYRIUM LABURNIPHILUM Oud. n. sp. — On the leaves of *Cytisus Laburnum*. — Nunspeet, Oct. 1898; Mr. BEINS.

Maculae amphigenae, orbiculares, oblongae vel irregulares, 2 ad 10 mill. latae, primo saturate-fuscae, postea pallescentes, postremo albidae, pallide-purpureo-marginatae, fragillimae. Perithecia epiphylla, epidermide velata, numerosa, minima, diam. $^1/_{10}$ mill. raro superantia, parte centrali paullo prominente et perforata. Sporulae breve ellipticae, $4^2/_3 \times 3^1/_2\ \mu$, pallide-olivaceae, in mucilaginem dilutam immersae, continuae, eguttulatae.

Differt a *C. olivaceo* praesentia macularum, peritheciorumque nec minus sporularum mensuris reductis.

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*Coniothyrium Psammae Oud. n. sp. — On the leaves of *Psamma littoralis* (= Ammophila arenaria). Cf. Hedw. XXXVII (1898) p. 177.

47. Coniothyrium pyxidatae Oud. n. sp. — On *Cladonia pyxidata*. — Valkenburg (L.) 1899; Mr. J. Rick.

Perithecia perfecte sphaerica, minutissima, vix $^1/_{10}$ mill. in diam., nigerrima; sporulae globosae vel subglobosae, dilute-olivaceae, vix $2^1/_3$ μ in diam., laeves, continuae, basi sua applanata vel truncatiuscula basidio crassiusculo brevissimo imposita.

Differt a *C. lichenicola* Karst. Symb. XX, 104, sporulis minoribus ($2^1/_3$ μ contra 3 μ), neque ovoideo-oblongis vel clavulatis, neque basi attenuatis, neque fuligineis, basidiis tandem brevioribus (2 μ contra 6 μ); a *C. Cladoniae* Ell. Everh. Sacc. in Syll. X, 268, peritheciis fere duplo minoribus ($^1/_{14}$ — $^1/_{10}$ contra $^1/_6$ mill.), non obconico-cylindraceis, supra subtruncatis, sporis dilutius tinctis, minoribus ($2^1/_3$ contra 3 μ), basidiis multo brevioribus (2 c. 6 μ).

48. Coniothyrium Tamaricis Oud. n. sp. — On the thin branchlets of *Tamarix gallica*. — Nunspeet, Oct. 22, 1898; Mr. Beins.

Perithecia numerosa, sparsa, parva ($^1/_{10}$ — $^1/_8$ mill.), globulosa, epidermide velata, prominentia, nigra. Sporulae ovatae, primo hyalinae, denique lutescentes, $7 \times 3^1/_2$ μ, guttula centrali elliptica insignes (Pl. IV, fig. 5).

Differt a *C. tamaricella* Brun. (Sacc. Syll. XIV, 923) sporulis pallidis neque „intense-olivaceis", et longioribus (7 μ contra $2^1/_2$ — 6 μ).

HAPLOSPORELLA Spegazzini.

49. Haplosporella Juglandis (Schum.) Oud. n. sp. (Naemaspora Juglandis Schumacher Flora Saellandiae II, 178; Cytospora Juglandis Rab. Kr. Fl. 148; Sacc. Syll. III, 267). — On the branches of *Juglans regia*. — Naaldwijk, Nov. 1866; the late Dr. J. E. van der Trappen.

Perithecia numero 4 ad 7 in stromate verruciformi, fere carbonisato, nigro, primo latente, postea in corticis vulnere large hiante, mill. 1 lato, peridermatis laciniis circumcincto, exposita. Sporulae globulosae ($2^1/_3$ μ in diam.) vel breve-ellipticae ($4^2/_3 \times 2^1/_3$ μ), continuae, fuliginosae, basidio brevi suffultae.

γ. *Hyalodidymae.*

ASCOCHYTA Libert.

*Ascochyta Acori Oud. n. sp. — On the leaves of *Acorus Calamus*. — Cf. N. K. A. 3, I, 496 et Hedw. XXXVII (1898) p. 177.

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*Ascochyta Euphrasiae Oud. n. sp. — On the stems of *Euphr. officinalis*. — Nunspeet, March 11, 1898; Mr. Beins. Cf. Ned. Kr. Arch. 3, I, 496.

*Ascochyta Grossulariae Oud. n. sp. — On the branches of *Ribes Grossularia*. — Cf. N. K. A. 3, I, 497 et Hedw. XXXVII (1898) p. 178.

50. Ascochyta Hypochoeridis Oud. n. sp. On the flower-stems of *Hypochoeris glabra*. Nunspeet, May 5, 1899; Mr. Beins.

Perithecia in maculis pallescentibus inordinate distributa, primo epidermide velata, prominentia, postea exposita, nigra, vertice perforata. Sporulae exacte cylindricae vel elongato-clavatae, ad polos rotundatae, vulgo rectae, rarius curvulae, hyalinae, imo quum in majorem copiam condensatae offenduntur, initio biocellatae, postea septo transversali dimidiatae. In sporulis clavatis pars anterior latior et paullo longior, pars posterior contra angustior et brevior (Pl. IV, fig. 6).

*Ascochyta Idaei Oud. n. sp. — On the branches of *Rubus idaeus*. Cf. N. K. A. 3, I, 497 et Hedw. XXXVII (1898), p. 178.

51. Ascochyta ignobilis Oud. n. sp. On the stems of *Alisma Plantago*. Nunspeet, March 13, 1898; Mr. Beins.

Maculae nullae. Perithecia primo epidermide velata, postea exposita, nigra, orbiculari-depressa, vertice perforata, 125—170 μ in diam. Sporulae cylindraceae, ad polos rotundatae, hyalinae, 9—12 $\times$ 3 μ, indistincte biocellatae, per longius tempus continuae, denique septo transversali aegre visibili, iodio addito vero mox optime distinguendo, dimidiatae.

A. ignobilis differt ab *A. Alismatis* Ellis et Everhart, Journ. of Mycol. 1889, p. 148 et Sacc. Syll. X, 307, quae in foliis offenditur, absentia macularum, peritheciis multo majoribus, sporulis paullo minoribus, praedilectione pro foliis.

52. Ascochyta Lactucae Oud. n. sp. — On the flower-stems and their ramifications of *Lactuca sativa*. — Naaldwijk, 1874; the late Dr. J. E. van der Trappen.

Perithecia in caespites aggregata, globuloso-depressa, epidermide velata, tandem exposita, nigra, vertice perforata, $^1/_7$—$^1/_6$ mill. in diam. Sporulae oblongae, hyalinae, ad polos rotundatae, biloculares, 12—15 $\times$ 3$^1/_2$ μ, medio superficialiter constrictae.

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53. ASCOCHYTA LEDICOLA Oud. n. sp. — On the leaves of *Ledum palustre*, together with *Thoracella Ledi* Oud. — Nunspeet, Sept. 29, 1898; Mr. BEINS.

Perithecia epiphylla, parum numerosa, inordinate distributa, $^1/_8$ mill. in diam., tandem vertice perforata. Sporulae fusiformes, hyalinae, ad polos acutae, biloculares, vix medio constrictae, $7—11 \times 2\ \mu$.

Ascochyta Ledi Rostrup (Sacc. Syll. X, 295), in *caulibus* Ledi palustris degens, sporulas fert oblongas, ad polos rotundatas, voluminosiores ($12—13 \times 3\ \mu$).

54. ASCOCHYTA LYSIMACHIAE Oud. n. sp. — On the stems of *Lysimachia thyrsiflora*, in company with *Phoma thyrsiflorae*. — Nunspeet, April 15, 1898; Mr. BEINS.

Maculae nullae. Perithecia laxe caespitosa, sub epidermidis portiuncula nigricante, in longitudinem protracta, p. m. prominente occultata, $^1/_3$ mill. in diam. Sporulae oblongae, ad polos rotundatae, hyalinae, bilocellatae, eguttulatae, medio non constrictae, $7—9^1/_3 \times 2^1/_3\ \mu$. Basidia ter longiora quam sporulae.

55. ASCOCHYTA MENYANTHIS Oud. n. sp. (non Lasch, neque Libert, quae ambae sub genere Septoria militant). — On the leaves of *Menyanthes trifoliata*, in company with *Septoria Menyanthis*.

Perithecia amphigena, vulgo tamen hypogena, una cum peritheciis *Septoriae Menyanthis* in maculis fuscis, satis extensis, polymorphis irregulariter distributa. Sporulae breve-cylindraceae, hyalinae, ad polos rotundatae, $14—19 \times 2^1/_3—3^1/_2\ \mu$, biloculares, loculis nitide 1- vel 2-ocellatis. Septum, vulgo p.m. obscurum, iodio addito statim conspicuum fit.

*ASCOCHYTA MATTHIOLAE Oud. n. sp. — On the pods of *Matthiola incana*. — Cf. N. K. A. 3, I, 497 et Hedw. XXXVII (1898) p. 178.

*ASCOCHYTA MISERA Oud. n. sp. — On the leaves of *Crataegus monogyna*. — Cf. N. K. A. 3, I, 497 et Hedw. XXXVII (1898) p. 178.

*ASCOCHYTA MYRTILLI Oud. n. sp. — On the dried sprigs of *Vaccinium Myrtillus*. — Cf. Hedw. XXXVII (1898), p. 317.

(To be continued).

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Botanics. — "*On the origin of new species of plants.*" By Prof. HUGO DE VRIES.

The fact that the species existing at the present moment are, as far as we observe, invariable, can but be brought into accordance with the theory of descent when admitting that periods of constancy alternate with periods of mutability. The former may last hundreds and thousands of years, the plant, as experience shows, continues the same, all the time. The latter have, hitherto, escaped all observation.

Probably, however, because they have not been sought for. And this again had its cause in our not having a right perception of what was to be found. For the prevalent opinion that species originate through very slow changes, is not favorable to such researches.

Side by side to this supposition, the so-called selection-theory, the possibility of a discontinuous origin of species was already recognised by DARWIN. The differences between closely allied species are in fact so slight that they may quite well appear at once. This idea has since continually found a few followers, in particular among paleontologists, but also among zoologists and botanists. Starting from this principle there is no longer any ground to suppose the origin of species as being beyond observation, and consequently, neither not to look for it.

My conclusion is: plants may, alternately with long periods of constancy, go through periods in which they produce one or more new species. On the other hand, each species has originated from another in such a period. And for this it is by no means necessary that the mother-species dissolves into the new ones, converts itself into these, it may continue, with all its former properties, quite unchanged.

If this view is right, the one thing necessary is to look for plants being in such a period of mutation. The chance of finding them is of course very slight, but this is no reason not to seek for them.

I have, in these researches, followed two methods. One consisted in direct observations on the wild growing-places; the other in the sowing out of seed collected from the natural habitat, or of seed from plants taken thence and brought into the garden. I sowed the seed in the garden on as large a scale as possible.

The result of this rather extensive research was the wished for. One species I found in a mutation-period. It is *Oenothera Lamarckiana*, introduced here, like *O. biennis* and *O. muricata*, from America.

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I sowed its seed for the first time in 1887 and at once obtained a new form, *O. lata*, and that in three specimens. In 1888 I again sowed seed and now on a larger scale. I once more obtained *O. lata*, in five specimens, and beside it a dwarf form, *O. nanella*, likewise in five, and a species with narrow, glossy leaves, *O. scintillans* in a single specimen. My culture amounted to about 15.000 seedlings, so that both first mentioned species had appeared at the rate of 1 specimen on 3000.

I have since repeated these sowings, first on as large, later, with more experience, on a smaller scale, and now possess the ninth generation of *O. Lamarckiana* in a state of mutation.

It produces both the first mentioned species nearly every year, the third from time to time.

Moreover, I have seen arising from it a series of other forms, formerly unknown, sometimes in a single, sometimes in various, sometimes, even, in rather numerous specimens. Thus the culture of 1895 produced on 14,000 seedlings, 1 *O. gigas*, 2 *O. leptocarpa*, 8 *O. rubrinervis*, 15 *O. albida* and 176 specimens of *O. oblonga*. These forms proved at once constant at the first sowing; they are still at present, after some generations of culture, just as they were at their first appearance. Besides, of the three last named, nearly every year new specimens arise from the primitive stock.

I have now, during my fifteen years' experiment, observed about a thousand mutations, in which twelve quite distinct, and mostly seed-fast species occurred. Moreover, there originated a number of other, indistinct, sterile, or insufficiently seed-fast types.

The rules followed in these mutations are:

1. The new species originate suddenly, without intermediate forms or any other preparation.

2. From the beginning they remain unchanged in the course of the generations.

3. They are mostly, at sowing, perfectly constant, from their very first appearance. A return to the mother-species, or atavism, I never observed in those cases. Exception *O. scintillans*, with strong atavism.

4. Among them is a dwarf-form, *(O. nanella)*, which may be taken as a variety; it behaves, however, just as the others. Those others deviate from one another, and from the mother-species, as much, and in some respects more, than closely allied, older species in this and other genera.

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5. They mostly appear in a great number of individuals, and repeatedly in a series of years.

6. The new properties are individually variable, according to QUETELET's law, like those of *O. Lamarckiana*. But between this variability and the mutation by which they took birth, there is no perceptible relation.

7. The mutations take place in various directions and not by preference in a determined one. Mostly they weaken the new species and so are disadvantageous *(O. albida)*, sometimes they are indifferent *(O. rubrinervis)*, sometimes probably favorable *(O. gigas)*. In many cases the fertility seems lessened, in others not at all.

The appearance of new species may be comprised in the form of a pedigree. The specimens repeating the type of *O. Lamarckiana*, then form the stock, of which each year the mutants are as many branches. In the pedigree below only these mutants are mentioned; the specimens obtained from their seed, which served me in the investigation after the constancy of the species, are left out.

The pedigree relates only to one of my experiments which was begun in 1886 with nine rosettes of two years' plants. These rosettes themselves were taken from the wild habitat, but had been removed in the autumn of the said year into the botanical garden, where in 1887 they flowered and bore seed.

Pedigree of Oenothera Lamarckiana.

Generation.	gigas	albida	oblonga	rubrinervis	Lam.	nanella	lata	scintillans
8th Generation 1899 annual.		5	1	.	1700	21	1	
7th Generation 1898 annual.		.	9	.	3000	11	.	
6th Generation 1897 annual.		11	29	3	1800	9	5	1
5th Generation 1896 annual.		25	135	20	8000	49	142	6
4th Generation 1895 annual.	1	15	176	8	14000	60	73	1
3rd Generation 1890/91 biennal.				1	10000	3	3	
2nd Generation 1888/89 biennal.					15000	5	5	
1st Generation 1886/87 biennal.					9			

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Physiology. — "*On muscle-tone*", *(abstract)*. By Dr. J. W. LANGELAAN (Communicated by Prof. T. PLACE).

The researches of late years have revealed a great system of afferent nerve fibres, partly originating in the muscle itself, partly in its adjacent tissues. Now it is highly probable, that the afferent nerve fibres belonging to the muscle, come into relation with the motor nerve cells in the anterior horn of the same muscle and form in this manner a muscle-reflex are on which muscle-tone depends.

To ascertain the extent of this tonicity, I chose the wellknown fact, that a normal muscle, the tendon of which is cut, undergoes abruptly a permanent shortening. This fact shows, that an elastic force resides in the tonic muscle. In order to determine this force, the distention of the muscle in rest was registered by means of a weight increasing with constant velocity. The muscle experimented on was the gastrocnemius of Rana esculenta, completely left in connection with its nerves and bloodvessels.

For the purpose of calculating the distensibility of the muscle from these tracings, the increase of length (Δ l) corresponding with a little augmentation of the charge (Δ p) was measured. The mean of two sets of measurements was taken as the amount of the distensibility at a certain moment, of which the differential coefficient $\left(\frac{dl}{dp}\right)$ is the symbol. This quotient, taken as measure of the muscle-tone, was therefore called the tonicity-quotient, and the tracings from which it was calculated named tonicity-curves.

From the experiments resulted, that, within the limits of the proof, succeeding increases of the charge forming terms of a geometrical progression, accorded with tonicity-quotients forming terms of an arithmetical progression; or formulated otherwise, that there existed a logarithmical relation between the value of the succeeding tonicity-quotients and the correspondent augmentations of the charge.

If the supposition made by FICK, HEIDENHAIN and afterwards by MOMMSEN, BENEDICENTI, GOWERS and SHERRINGTON is correct, that the terminations of the afferent nerve fibres in the muscle are stimulated by tension, it is evident that in my experiments the value of the distending weight must be a measure of this stimulus. Therefore if p be the amount of this weight $C_1 p$ must be the rate of stimulation, and the result consequent upon this excitement is the according value of the tonicity, symbolized by $C_2 \frac{dl}{dp}$. Applying, in this case,

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the law of FECHNER we are lead to the following connection:

$$C_1 p = e^{C_2 \frac{dl}{dp}} \qquad e \text{ base of the Nep. log.}$$

By integration this equation leads to the connection:

$$l = A.\, p + B.\, p.\ \text{lgn.}\ p.,$$

$$A = \frac{\text{lgn.}\ C_1 - 1}{C_2}$$

$$B = \frac{1}{C_2}$$

where l denotes the increase of the length of the resting muscle and p the augmentation of the charge.

The three tables added show how far this formula agrees with the facts.

A = 0.00724 B = — 0.00080		
p.	l. meas.	l. calc.
$3.0c_1$	0.013	0.017
6.2	0.030	(0.030)
12.6	0.060	0.057
25.4	0.102	(0.102)
33.5	0.121	0.129

A = 0.00925 B = — 0.00144		
p.	l. meas.	l. calc.
$3.0c_1$	0.017	0.020
6.2	0.036	(0.036)
12.6	0.064	0.062
25.4	0.104	(0.104)
30.9	0.116	0.119

A = 0.00777 B = — 0.00103		
p.	l. meas.	l. calc.
$3.0c_1$	0.016	0.019
6.2	0.035	(0.035)
12.6	0.065	0.063
25.4	0.110	(0.110)
27.1	0.113	0.111

Division of the spinal cord at the level of the second vertebra, did not change these results in any way.

Severing the tibial nerve above the knee-joint, the muscle is divided from its reflex-centre, the afferent and efferent paths being interrupted. The section is succeeded, within thirty seconds, by an allongation of the muscle, varying in different experiments from 0.3 to 1 pCt.; the distention-curves show quite a different form and the distensibility is diminished.

The beginning of these distention-curves is a straight line corresponding with an increase of the weight not beyond 5.5—9 gram;

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after a short part of transition, the distention-curve is represented by:

$$l = Ap + Bp^2$$

The tables added give an idea of the agreement.

A = 0.00441 B = — 0.00005		
p.	l. meas.	l. calc.
5.45c_1	0.0226	0.0229
6.45	0.0269	(0.0269)
7.45	0.0318	0.0306
12.1	0.0484	0.0468
13.1	0.0516	0.0500
14.1	0.0548	0.0531
25.4	0.0817	0.0807
26.4	0.0828	0.0825
27.1	0.0839	(0.0839)

A = 0.00633 B = — 0.000097		
p.	l. meas.	l. calc.
6.0c_1	0.0312	0.0313
7.0	0.0366	0.0368
11.0	0.0527	0.0531
12.0	0.0570	(0.0570)
13.0	0.0613	0.0608
17.0	0.0763	0.0735
18.0	0.0796	0.0771
19.0	0.0827	0.0798
23.0	0.0893	0.0894
24.0	0 0914	(0.0914)
25.0	0.0935	0.0933
30.0	0.105	0.100
31.8	0.107	0.102

A = 0.00499 B = — 0.00006		
p.	l. meas.	l. calc.
7.9c_1	0 0301	0.0323
8.9	0.0344	0.0359
9.9	0.0376	0.0363
15.0	0.0559	0.0561
16.0	0.0591	(0.0591)
17.0	0.0623	0.0621
23.0	0.0764	0.0773
24.0	0.0785	0.0795
25.0	0.0807	0.0816
32.1	0.0935	(0.0935)

From this it is clear, that the atonic muscle obeys the same empirical approximative formula of other elastic bodies.

In order to disturb only the afferent path, cocaine was injected into the spinal canal. The tracings obtained, all showed a rectilineal commencement, but this part of the curve never reached above a charge increase of 5.5 gram; for the further part it was found, that the variation of the distensibility grew slower than the increase of the charge, but faster than agreeable with a logarithmical relation.

To study the influence of the contraction of antagonistic muscles upon the tonicity of the agonists, I registered curves of the m. gastrocnemius, while during a certain interval of time the mm. tibialis anticus longus and peroneus were stimulated to a continuous contraction, by the current of a secondary coil. It was found, that the contraction of these praetibial muscles was succeeded by an

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increase of tonicity of the m. gastrocnemius of about 25 pCt. According to the definition of muscle-tone here adopted, the m. gastrocnemius became more distensible and this fact was already seen by BELL and afterwards found again by SHERRINGTON.

The variation of the tonicity becomes discontinuous, when the muscle contracting under a little charge, retains a residual shortening. In this case the tonicity-curve is built up of straight lines, at the end of each of those a part of the shortening is given back, while at the same moment the tonicity varies. The number of rectilineal part of which the curve is constituted, is almost constant for the same muscle, varying for different individuals. The length of each of these parts is mostly variable, but under favourable circumstances it is possible to obtain tracings in which they are nearly equal. In other cases doubtless compensations are found.

Amsterdam, September 1900.

Physiology. — "*On the determination of sensory spinal skin-fields in healthy individuals*". By Dr. J. W. LANGELAAN (Communicated by Prof. C. WINKLER).

What we know about this subject in man, was mainly due to pathological cases, and the schemas of HEAD were the most complete we had. But the physiological experiments by SHERRINGTON on Macacus rhesus, carrying on the investigations of TÜRCK and many others, and the minute dissections of BOLK on man, have given, independently of each other, results so accordant, that we can believe this problem to be solved in great features. Therefore not to add new facts, but only to show how it is possible to determine these fields in normal persons, this paper is communicated.

It was found in a case of locomotor ataxy by my colleague BEYERMAN, that in pricking the skin with a pin, there were narrow hyperalgetic bands, which closely seemed to follow the skin-field borders. I saw the same fact in another case of tabes and we interpreted them as the fields of overlap.

In order to research if these fields could be determined in a healthy person, I chose intelligent individuals, who could fix their attention for some time. I began to prick over the skin of the limb first crossing the mid-ventral line, great care being taken to prick in equal distances, with the same force and with equal intervals of time. Approaching the mid-line they all accuse a quickly increasing sensation of pain. Now I claimed them to note the just perceptible

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increase and marked this place with a blue pencil. Pricking from the opposite side in the same direction a second spot of pain increasing was fixed. In this manner, by all the persons I examined, the mid-dorsal and mid-ventral lines were easily found as bands extending along the axis of the limb, from a half to one centimeter breadth. In no case this crossed overlap on the limbs was found to be larger.

The limits of the fields formed by an anterior and posterior overlap were much more difficult to find, because the increase of the sensation was slighter and this difficulty grew in the vicinity of the joints. In harmony with this, it was found by SHERRINGTON, that the edge of the sensory skin-field is less abrupt at the anterior and posterior overlap than at the crossed overlap.

When the person under examination got tired, the limits of the fields of overlap came closer to each other; on the contrary, by repeating the experiment on the same person after a lapse of time, the borders became wider, because minuter differences were discriminated. The same relations are commonly met in determining the extent of the tactile spheres by means of the compasses of WEBER.

It is clear, that the fields of overlap fixed in this manner must be too small, for in the first place we know through the researches of SHERRINGTON, that the nerve supply from a single posterior root to its skin-field is less abundant at and near the edge of the field, and in the second place it is evident, that the increase of the sensation must reach a certain extent, before the difference is perceived.

I am convinced, that the subjectiveness of the method, exposes to many faults, and therefore I give only the photographical reproduction of the areas as found in some cases, without drawing any conclusions from it.

This method extended to the sensibility of temperature could perhaps give good results.

Amsterdam, September 1900.

All the persons examined were believed to be healthy individuals. The roman cyphers denote the number of the posterior root to which the skin-field probably belongs.

Fig. I. Inner side of the left arm. Person of research J. V., aged 27 years $^{21}/_{VIII}$. 2—3.30 P.M.

Fig. II. Outer side of the left arm; narrow overlap, p. of r. W. A. V., aged 25 years $^{23}/_{VIII}$ 2—3.30 P.M.

Fig. III. Outerside of the left arm; broad overlap. p. of r. M. H., aged 27 years $^{1}/_{IX}$ 2—3.20 P.M.

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J. W. LANGELAAN. "On the determination of sensory spinal skinfields in healthy individuals."

Fig. I.

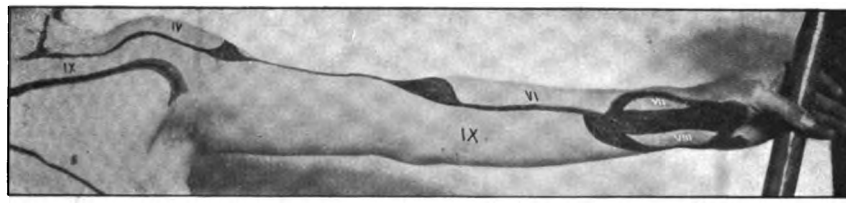

Fig. II.

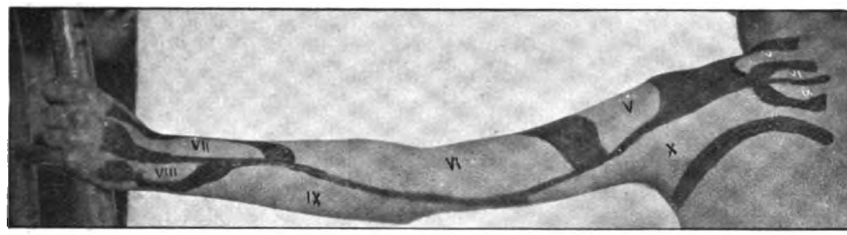

Fig. III.

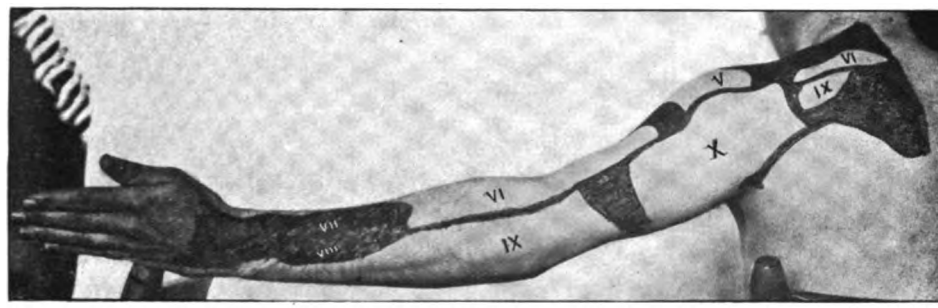

Fig. V.

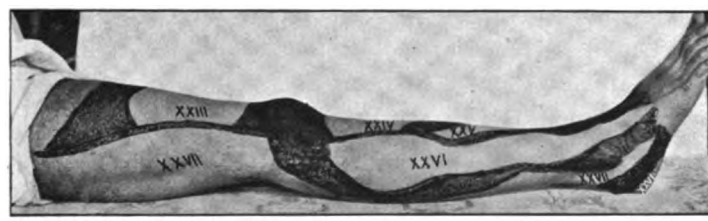

Fig. IV.

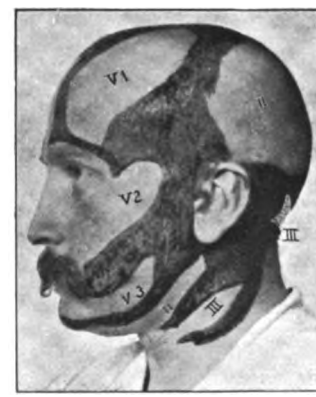

Fig. VI.

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Fig. IV. Left half of the chest; the skin round the nipple was at all hyperaesthetic and the border of this field was not certainly to determine. p. of r. J. v. d. L., aged 21 years $^{3}/_{IX}$ 10.30—11.30 A.M.

Fig. V. Outer side of the right leg; at the place marked with a cross skin field XXVII is divided in two parts by a broad overlap, p. of r. A. A. J., aged 27 years $^{25}/_{VIII}$ 1.30—3.20 P.M.

Fig. VI. Left half of the face. The field of overlap round the eye was not determined. The skin of the ear lays in a broad field of overlap. p. of r. E. W. de F., aged 24 years $^{6}/_{IX}$ 2—3 P.M.

Pathology. — "*Curious disturbances of the sensation of pain in a case of tabes dorsalis*". By D. H. Beyerman (Communicated by Prof. C. Winkler).

The following case was observed in the service of Prof. Winkler.

C., 52 years old, married to a husband, who made excesses in Baccho and in Venere, had three times abortus, one child born dead, three others dying a few days after their birth, and only one child alive. Seven years ago, she complained of diminishing of vision, afterwards of pains in the limbs and round the chest, the gait became staggering and difficulties in the deposition of urines with diarrhoea were observed.

On 13 July 1900, the following symptoms are stated.

Internal organs normal. Pupils equal, no reaction upon light and with convergention. Slight ptosis on both sides. Visus greatly diminished, large retraction of the field of vision on the right side, and atrophy of both optic nerves.

No ataxia, no paralysis in the upper limbs, only a slight paraesthesia in the ulnar fingers. Anaesthetic patches on the skin of the chest.

The ataxia in the lower limbs is very marked, increasing if the eyes are shut. Muscular force also diminished, the muscles are weak with marked hypotonicity of the joints. The knee-jerks and the reflexes of the tendo of Achilles are abolished, the plantar reflexes are present.

The sensation of pain has diminished in both legs, especially in the left, except on definite tender spots, where the slight pricking of a pin, or even a slight touch causes painful expression of the face.

The exact marking of those tender spots gives characteristic figures (photo's N°. 1 and N°. 2) in which they appear as joined together

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in regular bands, ressembling to the schemata of the root-innervation of the skin given by Prof. BOLK (photo's N°. 3 and N°. 4).

It seems difficult to explain the pathogeny of these hyperalgetic bands, but the nexus between their anatomical localisation and the distribution of the root-innervation of the skin seems very probable.

Geology. — *"The so called opake minerals in transmitted light"*. By Prof. J. L. C. SCHROEDER VAN DER KOLK.

(Read June 30, 1900,)

Among the outward characteristics of minerals, colour, as we know, occupies a principal place. With many minerals, more especially with the sulphides, the colour is so dark, that it often seems to be black. It is the powder however, which in many cases is the true indicator of colour. This powder is obtained generally in small but sufficient quantity by rubbing the mineral on an unpolished porcelain surface (the streak). Not a few apparent black minerals produce a coloured streak, but a good many others show one equally black or at least of as little colour as the mineral itself. Hence it is that with some dozens of minerals the streak is of little if of any value. It naturally suggests itself to attribute the absence of colour in the powder to the too great coarseness of the grains, which prevents them to become transparent. In fact in a great many cases, the rubbing down of the powder produces a distinct colour effect. It is easily reduced to smaller grains by rubbing out the streak with a hard object, a piece of quarz or with one of unpolished porcelain.

The following minerals are striking instances:

Pyrite pale brownish lilac; galena brown, a middle colour between bister an Indian ink. Clausthalite reddish brown; pentlandite lilac; covelline more or less brownish green; stibnite very bright yellowish brown; chalkopyrite brilliant deep violet; boulangerite reddish brown and bournonite brown.

It needs hardly be said, that colour cannot be described. Only by experimenting the thing will become clear. I may recommend here always to compare the colour with that of a rubbed out graphite-streak. To facilitate this experiment, I add a list of those minerals, which are more or less analogical as to the colour. Identity I however never met with and even tolerable resemblance of colours in two different minerals is very rare.

Green are molybdenite and covelline and bornite.

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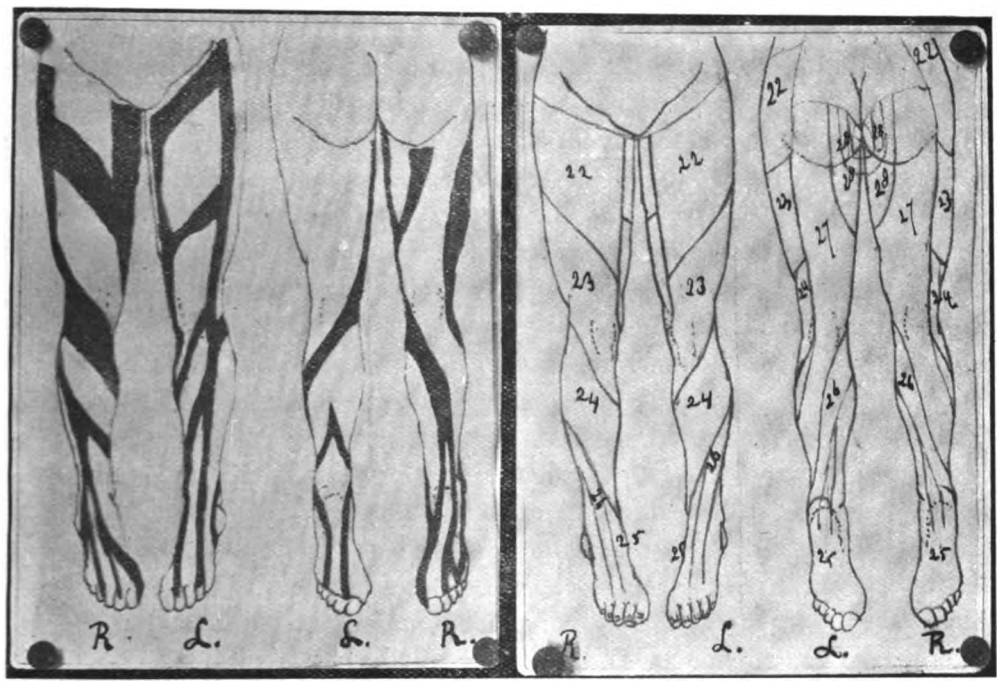
D. H. BEIJERMAN: Curious disturbances of the sensation of pain in a case of tabes dorsalis.



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Violet are chalkopyrite and pentlandite.

Pale brown, lilac tinged are pyrite, and more or less smaltine, cobaltine and ilmenite. The colour of the last mentioned mineral approaches some more reddish brown tetraedrites.

Pale yellowish brown are stibnite and jamesonite, whereas hausmannite and manganite in colour approach the following group.

Reddish brown are boulangerite and clausthalite: bournonite is less red and as to coulour forms a transition from the two last to stephanite, which approaches yellowish black.

Yellowish black are galena (greenish tinge) enargite and chalcosine, further berzilianite, argentite and berthierite. Finally anthracite might be mentioned here.

Pale brownish grey are magnetite and polianite; further stannine and corynite, although the streak of these last mentioned minerals is of a rather pure grey colour.

Still purer is the grey of graphite and pyrrhotine.

The above mentioned colours were an immediate result of the fineness of the particles growing transparent in consequence of that fineness. Still an other effect is produced by rubbing down the streak of certain minerals. I will just passingly mention it here, later I shall treat it more fully.

The effect I mean is most apparent in minerals which contain copper and best in cuprite. In rubbing out the brownish red streak the colour grows more and more greenish; at last to dissolve into a bluish green. However when shutting out the air with a drup of glycerine, no change of colours takes place. This same final colour is obtained in azurite and malachite.

I need hardly point out, that all those colours may be a great help in determining the so called opake minerals.

Mathematics. — On "*The spacial anharmonic ratio of curves ϱ^n of order n in the space S_n with n dimensions*". By Prof. P. H. SCHOUTE.

1. If on the curve ϱ^n in S_n, forming the subject of this short treatise, we take arbitrarily $n-1$ points A_i, $(i = 1, 2, \ldots n-1)$, we also determine thereby a space S_{n-2} containing these points, and we can assign the points of the curve one by one to the spaces S_{n-1} through S_{n-2} containing them. This gives rise to a correspondence one by one between the points of the curve and the spaces S_{n-1} of the pencil of spaces with the basis S_{n-2}, which proves the

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well-known theorem, that the genus of the curve ϱ^n is zero, and that we can just as well speak of the anharmonic ratio of four points of ϱ^n as of that of four points of a right line.

2. This simple consideration proves in general, that an invariable anharmonic ratio λ must be found by connecting any space S_{n-2} through $n-1$ variable points of the curve by spaces S_{n-1} with each of four fixed points A_1, A_2, A_3, A_4, which of course forms an extension of the well-known property of the conic ϱ^2 in the plane, that the quadruples of lines connecting a variable point P of the curve with four fixed points of the curve have an anharmonic ratio independent of P.

3. With this the generation of ϱ^n by means of n projectively related pencils of spaces S_{n-1} is closely connected. Moreover ensues from it that ϱ^n is determined by $n+3$ points. For, by dividing $n+3$ given points into two groups, one of n points and one of three, we can form by means of the n points of the first group n spaces S_{n-2} through $n-1$ points of the curve and after this determination of the n bases we can fix with the aid of the three points of the second group the projective correspondence between the n pencils of spaces S_{n-1}.

4. As is known the conic ϱ^2 in the plane can be considered as the locus of the points P which connected with four fixed points A_1, A_2, A_3, A_4 produce quadruples of lines of a definite anharmonic ratio λ, so that we can speak of the conic through A_1, A_2, A_3, A_4 containing the anharmonic ratio λ; by varying λ appears the pencil of conics filling the plane; of this pencil the points A_1, A_2, A_3, A_4 form the base. In like manner, if of a curve ϱ^n we give not $n+3$ but $n+2$ points $A_1, A_2, \ldots A_{n+2}$, we find instead of a single ϱ^n an $n-1$ fold infinite system of curves ϱ^n, filling S_n. And now arises the question whether it is not possible to indicate individually the curves of this $n-1$ fold infinite system by means of $n-1$ anharmonic ratios. This question must be answered in the affirmative. For, we have seen that on a given ϱ^n four given points represent a determined anharmonic ratio, and now out of the $n+2$ given points are to be formed by completing the triple $A_1\ A_2\ A_3$ with each of the remaining A_j to a quadruple $A_1\ A_2\ A_3\ A_j$, $(j=4, 5, \ldots n+2)$, exactly $n-1$ mutually independent anharmonic ratios $\lambda_j = (A_1\ A_2\ A_3\ A_j)$. From this follows for the present nothing but this that to a given curve ϱ^n through the $n+2$ given points belongs a definite set of anharmonic

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ratios λ_j, whilst on the other hand the possibility is not excluded that inversely to a given set of anharmonic ratios λ_j belongs more than one curve ϱ^n passing through $n+2$ given points. It is however easily proved that all those curves ϱ^n belonging to a given set of anharmonic ratios — supposing there be more than *one* — are projected from A_{n+2} by the same conical space of order $n-1$. For if we project the figure considered, from the point A_{n+2} upon the space S_{n-1} determined by $A_2, A_3, \ldots A_{n+1}$, the curves ϱ^n through $A_1, A_2, \ldots A_{n+2}$ with the anharmonic ratios $\lambda_4, \lambda_5, \ldots \lambda_{n+2}$ in S_n are transformed into the curves ϱ^{n-1} through $A'_1, A_2, \ldots A_{n+1}$ with the anharmonic ratios $\lambda_4, \lambda_5, \ldots \lambda_{n+1}$ in S_{n-1}. And by repeating this reduction, passing from the applied space S_{n-1} to the space S_{n-2} determined by $A_2, A_3, \ldots A_n$ etc. till we arrive at the plane of projection $A_2\ A_3\ A_4$ where the original point A_1 may finally arrive in A''_1, two curves ϱ^n which pass through the $n+2$ given points, belong to the anharmonic ratios $\lambda_4, \lambda_5, \ldots \lambda_{n+2}$ and are projected from A_{n+2} by different conical spaces of order $n-1$, will finally be transformed into two different conics through A''_1, A_2, A_3, A_4, to which belongs the same anharmonic ratio λ_4. This being impossible the different curves ϱ^n through the $n+2$ given points which might belong to the given set of anharmonic ratios $\lambda_4, \lambda_5, \ldots \lambda_{n+2}$, must be projected from A_{n+2} by means of the same conical space. And what is true for the point A_{n+2} is applicable to all the remaining given points. So all curves ϱ^n which may belong to a given set of anharmonic ratios $\lambda_4, \lambda_5, \ldots \lambda_{n+2}$, being projected from all points A_i, $(i = 1, 2, \ldots n+2)$, by the same conical spaces, must coincide. So in general we find:

"We can determine in S_n a curve ϱ^n passing through any $n+2$ points A_i, $(i=1, 2, \ldots n+2)$, by indicating the $n-1$ anharmonic ratios $\lambda_j = (A_1\ A_2\ A_3\ A_j)$, $(j = 4, 5, \ldots n+2)$. And these anharmonic ratios assuming all possible values, the determined curve ϱ^n generates the $n-1$ fold infinite linear system with the base $A_i, A_2, \ldots n+2$, filling the space S_n, which system is of course projectively related to the likewise $n-1$ fold infinite linear system of the anharmonic ratios $\lambda_4, \lambda_5, \ldots \lambda_{n+2}$, or in other words to the linear system of points in a space S_{n-1} of which the coordinates are given by means of these systems of values."

The preceding proof wants some completion. We might ask, a. o. with a view to the structure of the anharmonic ratios, where on one side A_1, A_2, A_3 and on the other side $A_4, A_5, \ldots A_{n+2}$ play different parts, whether we are allowed to extend to all points A_i what has been found true for A_{n+2}. Yet leaving alone whether it be necessary to know that all points A_i behave in this respect alike, it is easy to

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see at once, that the difference between the points of the two groups is in this respect but an apparent one. For by giving the $n-1$ anharmonic ratios $(A_1 A_2 A_3 A_j), (j = 4, 5, \ldots n+2)$, all anharmonic ratios of quadruples of points A_i are determined. For, if on a right line l, corresponding point by point to ϱ^n, we assume arbitrarily the points belonging to A_1, A_2, A_3, the given anharmonic ratios determine the points belonging to $A_4, A_5, \ldots A_{n+2}$; so on l the n corresponding points and thus all the anharmonic ratios are known.

5. Probably it is recommendable to call the complex of the $6\frac{(n+2)(n+1)n(n-1)}{1 \cdot 2 \cdot 3 \cdot 4.}$ anharmonic ratios, determined by $n-1$ mutually independent ones out of them, simply a *spacial* anharmonic ratio and to represent it by the symbol $\lambda_{(n-1)}$. We can then say, that the $n-1$ fold infinite linear system of curves ϱ^n with $n+2$ points A_i as base is projectively related to that spacial anharmonic ratio, in so far that a curve of the system corresponds to a definite spacial anharmonic ratio and reversely. By this the analogy of the obtained result with the special case $n=2$ becomes as great as possible.

6. The above led us to the following theorem of cyclic inversion, which we shall first indicate for the special case $n=3$ of our space. The net of the skew cubics ϱ^3 is then given by its five base points. If we put

$$(A_1A_2A_3A_4) = \lambda_0, \quad (A_2A_3A_4A_5) = \lambda_1, \quad (A_3A_4A_5A_1) = \lambda_2,$$
$$(A_4A_5A_1A_2) = \lambda_3, \quad (A_5A_1A_2A_3) = \lambda_4,$$

where $(PQRS)$ always stands for

$$\frac{PR}{QR} : \frac{PS}{QS},$$

then the question rises by which recurrent relation the five quantities $\lambda_i, (i=0, 1, 2, 3, 4)$, are connected. By direct reckoning we find

$$\lambda_{m+2} = \frac{\lambda_{m+1}}{\lambda_m(\lambda_{m+1}-1)},$$

where $m, m+1, m+2$ are to be replaced by their remainders after division by five; and really by repeated substitution we arrive at $\lambda_{m+5} = \lambda_m$. Of course in the general case of an arbitrary n a result will be obtained of the form

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$$\lambda_{m+n-1} = f(\lambda_m, \lambda_{m+1}, \ldots \lambda_{m+n-2}) .$$

However, the definition of the form of the function f we leave to others.

7. We shall point out a few particularities which already appear when we restrict ourselves to space with three dimensions.

In the following way the net of the skew cubics ϱ^3 through five points is deduced from considerations on conics and cones.

If A, B, C, D, E are five points given arbitrarily in space, the locus of the vertices T of the cones $T(A,B,C,D,E)$ through these points, on which the edges $T(A, B, C, D)$ represent a definite anharmonic ratio λ, is the cone $E_\lambda(A,B,C,D)$ through A,B,C,D with vertex E, on which the edges passing through A, B, C, D determine the anharmonic ratio λ. And if λ assumes all possible values this cone generates the pencil with EA, EB, EC, ED as base edges, filling the space.

For, if P is an arbitrary point of $E_\lambda(A, B, C, D)$, then according to definition

$$P(AE, BE, CE, DE) = \lambda$$

and this is identical with

$$E(AP, BP, CP\, DP) = \lambda.$$

If A, B, C, D, E are again five points given arbitrarily in space, the locus of the vertices T of the cones $T(A,B,C,D,E)$ through these points, on which $T(A, B, C, D)$ and $T(A, B, C, E)$ represent respectively the anharmonic ratios λ and μ, is the skew cubic $\varrho^3_{\lambda,\mu}$ through A, B, C, D, E, forming with the line DE the complete intersection of the cones $E_\lambda(A, B, C, D)$ and $D_\mu(A, B, C, E)$. And if λ and μ assume all possible values, this curve generates the net with the base A, B, C, D, E; this net filling the space is projectively related to the points (λ, μ) of a point-field.

The anharmonic ratios $T(A, B, C, D)$ and $T(A, B, C, E)$ on the cone $T(A, B, C, D, E)$ being identical with the anharmonic ratios (A, B, C, D) and (A, B, C, E) on the curve $\varrho^3_{\lambda,\mu}$, this result is nothing more but at the same time nothing less than the special case $n=3$ of the general result obtained before. And from this we could have gone on to the case $n = 4$ in order to prove the anticipated general result by the conclusion from n to $n + 1$. It occurred to us however that the deduction given above of the general result is shorter and clearer.

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8. By assuming between λ and μ the bilinear relation

$$p\lambda\mu + q\lambda + r\mu + s = 0$$

we form a projective correspondence between the cones $E_\lambda(A,B,C,D)$ and $D_\mu(A,B,C,E)$. So we find.

"The locus of the curves $\varphi^3_{\lambda,\mu}$, for which λ and μ satisfy a given bilinear relation, is a surface F^4 cf order four, on which the two triples of lines DA, DB, DC and EA, EB, EC are simple lines, the points A, B, C are double points and DE is a double line. All these different surfaces F^4 form a threefold infinite linear system, projectively related to the linear system of the rectangular hyperbolae, represented by the equation of correspondence, if λ and μ indicate the rectangular coordinates of a point in the plane."

"If in particular $p=0$, then $\lambda=\infty$ and $\mu=\infty$ correspond to each other and likewise the pairs of planes $E(AD, BC)$ and $D(AE, BC)$. Then the surface F^4, passing through BC, breaks up into the plane ADE and a surface F^3, i. e. the locus of the curves $\varphi^3_{\lambda,\mu}$ is then an F^3 through the edges of the tetrahedron $BCDE$. All these surfaces pass through A and have B, C, D, E as double points; so they form a net of course projectively related to the net of the right lines $q\lambda + r\mu + s = 0$."

"If at the same time $q=0$, we then find $\lambda=\infty$ and $r\mu+s=0$, so that F^4 breaks up into the pair of planes $E(AD, BC)$ and a cone $D_\mu(A, B, C, E)$. By the addition of $q=0$ a new plane i. e. BCE has separated from F^4."

"The linear system of the surface F^4 contains a net of surfaces F^3 and two pencils of cones."

Also analytically we can easily find that the surfaces F^4 having DE as double line, A, B, C as double points and passing through the triples of lines $D(A,B,C)$, $E(A,B,C)$ form an at least threefold infinite series. Firstly we learn out of the equation.

$$z^2\varphi_2(x,y) + zt\psi_2(x,y) + t^2\chi_2(x,y) + z\xi_3(x,y) + t\eta_3(x,y) + \zeta_4(x,y) = 0$$

of a surface $f_4(x,y,z,t)=0$ of order four with the right line $x=0$, $y=0$ as double line, that of the 35 coefficients of the complete equation only

$$3 \quad + \quad 3 \quad + \quad 3 \quad + \quad 4 \quad + \quad 4 \quad + \quad 5$$

or 22 are extant, so that the compound condition of having DE as a double line is equivalent to 13 simple ones. The condition of

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having A, B, C as double points and that of passing through six given lines count respectively for 12 and at most for 6 simple ones, so that at least 3 remain at our disposal. Only if each surface F^4 with DE as a double line and A, B, C as double points, which is brought through five of the six lines, contained by that already also the sixth — a peculiarity which appears as will be seen in the following series of surfaces — the number of conditions to be disposed of could become greater than 3; so this peculiarity does not appear here.

It is also easy to see that the surfaces F^3 through A with the double points B, C, D, E form a twofold infinite series. For, the surfaces $f_3(x, y, z, t) = 0$ with the vertices of the tetrahedron of coordinates as double points form a linear system

$$a\,yzt + b\,ztx + c\,txy + d\,xyz = 0,$$

etc.

9. If we assume in space six given points A, B, C, D, E, F, we arrive in the following way at a generation of skew biquadratics:

"The locus of the common vertices T of the cones $T(A, B, C, D, E)$ and $T(A, B, C, D, F)$, on which the four edges $T(A, B, C, D)$ determine respectively the anharmonic ratios λ and μ, is the skew biquadratic $\varrho^4_{\lambda,\mu}$ through A, B, C, D forming the complete intersection of the cones $E_\lambda(A, B, C, D)$ and $F_\mu(A, B, C, D)$; of this curve E and F are two of the four vertices of cones containing it. And if λ and μ assume all possible values this ϱ^4 generates the net with the base A, B, C, D and the vertices E, F; this net filling the space is a. o. projectively related to the point-field (λ, μ)."

"The locus of the curves $\varrho^4_{\lambda,\mu}$, for which λ and μ satisfy a given bilinear relation, is a surface F^4 of order four, having the points A, B, C, D, E, F as double points and containing the quadruples of lines $E(A, B, C, D)$ and $F(A, B, C, D)$. All these surfaces F^4 form again a threefold infinite linear system, projectively related to the linear system of the rectangular hyperbolae represented by the equation of correspondence."

Some difficulty arises regarding the proof, that the surfaces F^4 found here really represent a threefold infinite series. For, the condition first of having six double points and secondly of passing through eight lines connecting four of these points with the remaining two is equivalent to 24 and apparently to 8 simple conditions more; from which would ensue, that only two simple conditions remain at our disposal. This difficulty can be removed only by the supposition, that each surface F^4 with the double points A, B, C, D, E, F

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passing through seven of the eight lines (E, F) (A, B, C, D) also contains the eighth. In reality the surface of the series degenerated into four planes show that the series is threefold infinite. For of the nine degenerated surfaces

I	II	III	IV	V	VI	VII	VIII	IX
EAB	EAB	EAB	EAC	EAC	EAC	EAD	EAD	EAD
ECD	ECD	ECD	EBD	EBD	EBD	EBC	EBC	EBC
FAB	FAC	FAD	FAB	FAC	FAD	FAB	FAC	FAD
FCD	FBD	FBC	FCD	FBD	FBC	FCD	FBD	FBC

the individuals of each of the triples (I, II, III), (IV, V, VI), (VII, VIII, IX), (I, IV, VII), (II, V, VIII), (III, VI, IX) belong to a same pencil, as is shown by the identity

$$(x-y)(z-t)+(x-z)(t-y)+(x-t)(y-z)=0.$$

So I, II, IV, V are four degenerations no three out of which belong to a pencil. Moreover the fourth not belonging to the net determined by the others — for I, II, IV contain AB and CD and these lines do not lie on V — they form a linear system of threefold infinity.

10. For seven points A, B, C, D, E, F, G given arbitrarily in space we have farthermore:

"Four vertices T are to be found for which the common edges $T(A, B, C, D)$ determine respectively on the three cones $T(A,B,C,D,E)$, $T(A, B, C, D, F)$, $T(A, B, C, D, G)$ the anharmonic ratios λ, μ, ν. These four points form with A,B,C,D the eight points of intersection of the three cones $E_\lambda(A,B,C,D)$, $F_\mu(A,B,C,D)$, $G_\nu(A,B,C,D)$. And if λ, μ, ν assume all possible values, this quadruple of points generates a biquadratic involution of quadruples of points filling the space and projectively related to the points (λ, μ, ν) of space."

According to the general character of the involution a quadruple of points P, Q, R, S is determined by one of its points; if P is given the cones $E(A, B, C, D, P)$, $F(A, B, C, D, P)$, $G(A, B, C, D, P)$ are determined and likewise the three other new points of intersection. In fact, we have not to deal with *all* quadruples of points completing A, B, C, D to eight *associated* points, in which case we might arbitrarily assume seven out of the eight points, but only with those octuples A, B, C, D, P, Q, R, S, for which E, F, G are three ver-

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tices of quadratic cones containing them. Of course a great number of problems appear immediately. We can ask what Q, R, S generate together when P describes a right line or a plane, what the locus is of the quadruple of points under the condition that one of six connecting lines passes through a given point or intersects a given line, etc. In order not to be too prolix we shall discuss but two other loci.

Of these the first is connected with the trilinear equation

$$k\lambda\mu\nu + l\mu\nu + m\nu\lambda + n\lambda\mu + p\lambda + q\mu + r\nu + s = 0$$

between λ, μ, ν. We find:

"The locus of the quadruples of points of intersection of the three cones $E_\lambda(A, B, C, D)$, $F_\mu(A, B, C, D)$, $G_\nu(A, B, C, D)$, for which λ, μ, ν satisfy a given trilinear equation, is a surface of order six with A, B, C, D as threefold points, E, F, G as double points and the three quadruples of lines obtained by connecting each of three points E, F, G with the four points A, B, C, D as simple lines. All those surfaces F^6 form a sevenfold infinite linear system, projectively related to the in like way sevenfold infinite system of cubic surfaces represented by the equation of correspondence."

Here is again immediately shown, that the found surfaces F^6 form an at least sevenfold infinite series. For of the 83 simple conditions determining an F^6 the four threefold points take 40, the three double points 12 and the 12 right lines at most 24, so that at least 7 remain at our disposal. The system of the surfaces F^6 being really sevenfold infinite, from this ensues reversely that the determining quantities — threefold points, double points and simple lines — represent mutually independent data.

Secondly we look for the locus of the quadruples of points of intersection, for which λ, μ, ν are equal to one another. We find:

"The locus of the quadruples of points of intersection of the three cones $E_\lambda(A, B, C, D)$, $F_\mu(A, B, C, D)$, $G_\nu(A, B, C, D)$, for which λ, μ, ν are equal to one another, is a skew sextic not passing through A, B, C, D, E, F, G."

According to the above the locus of the intersection $\varrho^4_{\lambda,\mu}$ of $E_\lambda(A, B, C, D)$ and $F_\mu(A, B, C, D)$, for which $\lambda = \mu$, is a surface F^4 passing through the two quadruples of lines $E(A, B, C, D)$ and $F(A, B, C, D)$ with the double points A, B, C, D, E, F, which passes — the values $0, 1, \infty$ of λ corresponding to equal values of μ — likewise through the edges of the tetrahedron $ABCD$.

In like manner the locus of the intersection of $E_\lambda(A, B, C, D)$ and

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$G,(A,B,C,D)$, for which $\lambda = \nu$, is an F^4 with the double points A, B, C, D, E, G passing through the quadruples of lines $E(A,B,C,D)$ and $G(A,B,C,D)$ and the edges of the tetrahedron $ABCD$. Of the total intersection φ^{16} of these surfaces, having A, B, C, D, E as fourfold points, the ten right lines connecting the points A, B, C, D, E two by two, separate; so has been proved what was asserted.

Botanics. — "*Preservatives on the stigma against the Germination of Foreign Pollen.*" By Dr. W. BURCK. (Communicated by Professor HUGO DE VRIES.)

It is well known that the pollen of many plants gets destroyed as soon as it comes into contact with water. The both coats (exine and intine) are then seen to burst, while the contents stream out vigorously [1]).

Further it is known that frequently pollen is successfully brought into germination in sugar solutions at different degrees of concentration, or also in gelatin, agar-agar, gum, dextrine etc., or in mixtures of these substances with sugar [2]).

For number of pollen species, however, there has not yet been found, hitherto, a solution in which germination was observed (many *Compositae*, *Umbelliferae*, *Urticaceae*, *Malvaceae*, *Ericaceae*, and many others).

The idea that chemical substances occurring in the moisture of the stigma would here play a part, has been frequently expressed, among others by MOLISCH [3]), in 1892, who inferred it from the fact

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[1]) On the relation of pollen to water compare, among others, BENGT LIDFORSS, Zur Biologie des Pollens. Pringsheim's Jahrbücher Bd. XXIX, 1896, pag. 1—39.

HANSGIRG, Beiträge zur Biologie und Morphologie des Pollens. Sitzungsber. der K. Böhm. Gesellsch. 1897, XXIII.

BENGT LIDFORSS, Weitere Beiträge zur Biologie des Pollens. Pringsheim's Jahrb. Bd. XXXIII, 1899.

[2]) See, among others, VAN TIEGHEM, Recherches physiologiques sur la végétation libre du pollen et de l'ovule. Annales des sc. nat. Bot. 5e série, tom. XII, 1872.

L. KNY, Sitzungsber. d. botanischen Vereines d. Provinz Brandenburg XXIII, 1881.

E. STRASBURGER, Neuere Untersuchungen über den Befruchtungs-Vorgang bei den Phanerogamen etc. Jena 1884.

E. STRASBURGER, Ueber fremdartige Bestäubung. Pringsheim's Jahrb. für w. Botanik Bd. XVIII, 1886.

H. MOLISCH, Zur Physiologie des Pollens, mit besonderer Rücksicht auf die chemotropischen Bewegungen der Pollenschläuche. Sitzungsber. der math. naturw. Classe der K. Akademie der Wissensch. Wien Bd. CII, Abth. I, 1893.

[3]) MOLISCH, l.c. pag. 429.

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that the pollen of *Azalea*, which could not be brought into germination in water, formed beautiful pollen-tubes when, together with the pollen, a stigma of *Azalea* was introduced into the drop of water.

To me, also, it has seemed probable, for years already, that pollen, which did not germinate in water or sugar solutions, wanted a special chemical stimulus to call forth the process of germination, and that in the either or not being present of such a chemical substance in the liquid of the stigma, in some cases the explanation might be found of the striking fact, that often the pollen cannot germinate on the stigma of a plant, which stands in close relationship to the plant producing the pollen, while it germinates very well on the stigma of a plant belonging to a systematically distant family [1]).

Already in 1889 I thought this might be inferred from the facts following. The pollen of *Mussaenda rufinervis*, *M. frondosa*, *M. Teijsmanniana*, *M. Afzelii*, *M. Reinwardtiana* and *M. cylindrocarpa*, belong to those species of pollen which resist the action of water and are not prejudiced by it, but which do not, however, pass into germination in it.

When now this pollen is introduced into a drop of destilled water, in which is at the same time put a stigma of the plant, nearly all the pollen-grains will begin, within the space of two hours, to form tubes, which rather quickly attain a considerable length.

It is not necessary therefore to use the whole of the stigma; the germination sets in as well if only a half, a fourth, or an eighth part is put in the drop of water, and I even saw distinct germination on addition of $^1/_{16}$ part of the stigma.

The same experiment to make pollen germinate in the thus diluted stigma-liquid of the same plant, succeeded for many species of *Pavetta* and further for *Pentas carnea*, *Eriostemma floribunda*, four species of *Begonia*, for *Uvaria purpurea*, *U. hirsuta*, *Torenia Fournieri*, and for *Murraija exotica*, plants belonging to the *Rubiaceae*, *Begoniaceae*, *Anonaceae*, *Scrophulariaceae* and *Rutaceae*.

With a great many other plants, however, the experiment did not succeed.

Furthermore I had found that for *Mussaenda* it did not matter whether the stigma of the same species was used, or that of another species of the genus.

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[1]) Strasburger, Ueber fremdartige Bestäubung l.c.

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The pollen of *M. rufinervis* germinates as well in the dilute liquid of *M. frondosa* and *M. cylindrocarpa* as in that of its own species, and pollen of *M. frondosa* could also be brought into germination in the stigma-liquid of *M. rufinervis* and *M. cylindrocarpa*, whilst the pollen of *M. cylindrocarpa*, *M. Reinwardtiana* and *M. Teijsmanniana*, germinated besides in the stigma-liquid of *M. rufinervis*.

For the different species of *Pavetta* this was otherwise.

I succeeded indeed in causing the pollen of *Pavetta javanica* to germinate in destilled water in the presence of a stigma of *P. javanica* and *P. fulgens*, but not in the dilute stigma-liquid of *P. longipes*, *P. grandiflora*, *P. coriacea* and *P. pauciflora*.

The pollen of *Pavetta grandiflora* germinated only in presence of a stigma of its own species and of *P. fulgens*, but not with a stigma of *P. javanica*, *P. longipes*, *P. coriacea* and *P. pauciflora*.

That of *Pavetta coriacea* could not be brought into germination at all in this way, not even when using the stigma of *P. coriacea* itself.

It was also proved that the pollen of *Mussaenda cylindrocarpa* did not germinate in the dilute stigma-liquid of *Pavetta grandiflora* and the pollen of *Mussaenda rufinervis* not in that of *Gardenia curvata*, etc. All this points to the presence in the fluid of the stigma of substances which possess the power to bring about the process of germination, and gives also cause to suppose that for distinct genera and also for distinct species of the same genus, those substances may be distinct too. Since I occupied myself with this investigation, the pollen has repeatedly been the object of interesting researches, as well with regard to its relation to water (KERNER, LIDFORSS, HANSGIRG), and to the negative aerotropism, which may be observed in pollen-tubes (MOLISCH), as to the chemotropical action exerted by the stigma and by special chemical compounds on the pollen-tubes.

It is not impossible that sometimes the same substances which exert a chemotropical influence on the *once formed* pollen-tube, also possess the faculty to excite the latent germinal power of the pollen-grains, but certain it is not; in any case, it has not yet been proved to be so.

If a stigma of *Narcissus Tazetta* is passed into a drop of sugar-gelatin solution, together with some pollen of this plant, then, as MOLISCH has pointed out, the tubes formed are attracted by the stigma and also by the section-face of the style, but the germination of the pollen itself is not influenced by the stigma; the process of germination is accomplished also without a stigma, if only the

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Narcissus-pollen is introduced into the 7 pCt. sugar solution referred to [1]).

The influence of the stigma is first felt when the tubes are formed, and after all appearance the curving towards the stigma, in this case at least, reposes on a growth towards the nutrient source (trophotropism) of a pollen-tube, formed from the reserve-substances of the pollen-grain.

The last research of LIDFORSS [2]) proved that the stigma can in this experiment be replaced by organs of foreign plants, for instance by bits of *Allium*-root, which made him suppose that a substance, largely spread in the vegetable kingdom, was here concerned. Fragments of diastase act in the same way and, as was nearer indicated, it is not the diastase as such, the starch-converting principle, but the albumen occurring in the preparations, from which goes out the chemotropical influence.

So, these things should not be confounded; the chemical substances possessing the faculty to call forth the process of germination are not, — at least not here — the same that occasion a chemotropical curvation of a once formed pollen-tube.

An investigation of chemotropical curvations under the influence of a stigma was not in my way. Nor was the way in which the germination experiments were performed, — namely in a medium in which the soluble constituents easily diffunded from the stigma-moisture, adapted to observations in this direction.

My object was exclusively to examine in how far pollen, not passing into germination in water or in sugar solutions, required a special chemical substance to call forth the germination. For I put myself the question whether STRASBURGER's opinion that on the stigma no preservatives were present to prevent the germination of foreign pollen, was not taken in too general a sense?

After the said preliminary experiments had pointed out the presence in the stigma-fluid of special chemical compositions, under whose influence the germination was brought about, I tried to find a substance able to exert on the pollen of these different plants, the same influence as the stigma-fluid.

This research has led to the following results:

It lay at hand first of all to think of some organic acid, not only because the stigmas react feebly acidly, but in particular on

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[1]) MOLISCH l. c. p. 427.

[2]) Bot. Centralbl. No. 11, 1900, p. 373.

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account of the well-known influence of organic salts and acids on the spermatozoids of ferns and of *Selaginella* [1]).

All my efforts, however, to find a solution of tartaric acid, oxalic acid, or malic acid, able to make the pollen of *Mussaenda rufinervis* germinate, remained unsuccessful [2]).

Since it is become known that MOLISCH, led by the same course of thought, tried in 1892, by means of organic acids and salts, to call forth the development of tubes in pollen of some *Compositae*, *Umbelliferae*, *Urticaceae*, *Malvaceae* and *Ericaceae*, which could not be caused to germinate in water, gelatin, sugar, glycerine, or gum, and that he indeed succeeded in so far as regards that of *Azalea indica*, *Rhododendron ponticum*, and *R. arboreum*. In solutions of 1—0,05 calcium malate and of 0.01 pCt. malic acid, germination was observed [3]).

The other pollen species were quite insensible to these stimuli.

As little as the pollen of *Mussaenda*, that of different species of *Pavetta*, *Begonia* and *Pentas carnea*, was to be brought into germination in acids or salts.

From the acids I turned to the sugars and allied substances and then it became evident that it was impossible to cause the *Mussaenda*-pollen to germinate in solution of *saccharose*, whichsoever degree of concentration this solution might have. I used solutions of 0.05 pCt. mounting to 40 pCt.

No more were *Mannite* and *Dextrose* able to cause germination. Experiments with *Asparagine* and *Dextrine*, too, led to no results.

When, however, the slightest trace of levulose was added to the water, the process of germination set in within the time of two hours and soon the tubes proved as long and as beautiful as at the germination in dilute stigma-liquid.

Here it was perfectly indifferent whether *levulose* was added to the destilled water, or to the solutions of the said sugars in different degrees of concentration, or to a solution of gelatin. *Levulose* proved thus to exert the same influence on the pollen-grains as the stigma.

That the chemical substance which diffunds from the stigma-liquid in the drop of water should contain *levulose*, is, of course, not ascertained hereby; other substances also occurring in the stigma-liquid

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[1]) PFEFFER, Locomotorische Richtungsbewegungen durch chemische Reize. Unters. aus dem bot. Institut zu Tübingen Bd. I, Heft 3.

[2]) The experiments were performed with solutions of 0.2 pCt. to 0.0025 pCt.

[3]) MOLISCH, l. c. p. 429.

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might exert the same influence on the pollen-grains of *Mussaenda*. Presently it will become evident, at the mentioning of a related experiment, that it is necessary to be cautious with such an identification.

The research showed further that the pollen of other species of *Mussaenda* behaved towards sugar solutions just in the same way as that of *M. rufinervis*; from the facility with which the pollen of these species germinated in each other's dilute stigma-liquid, this might be expected.

The pollen of *Begonia* corresponds, regarding its relation to sugar solutions, in many respects with that of *Mussaenda*, but in this genus important deviations occur with regard to the behaviour of the pollen to water.

That of *Begonia gorgocensis* namely, germinates already in destilled water, while that of *B. Deppii*, *B. semperflorens* and *B. imperialis* does not try to form tubes in water. Of all four examined species the pollen germinates, however, easily in the presence of a stigma in the drop of water. But here I should observe that it is not beforehand to be said with certainty whether newly collected pollen of *Begonia gorgocensis* will come into germination in destilled water or not.

Repeatedly in the germination experiments the phenomenon occurred that the pollen of this *Begonia*, having one day formed tubes in the drop of water, the next day did not manifest a trace of tube-development, although it was taken from the same plant.

This is a particularity which I later found not to be rare in other species of pollen neither.

All botanists who have occupied themselves with the germination of pollen, have likewise experienced that its relation to water is not always the same by far.

A slight difference in the humidity of the surrounding air can be the cause, not only that pollen which, under normal circumstances is resistent to the influence of water, when brought into contact with it bursts immediately, but also that pollen, which germinates in destilled water, cannot be brought into germination at a deviating humidity of the air. Elaborate informations thereabout have of late been given by BENGT LIDFORSS in PRINGSHEIM's Jahrbücher, Bd. XXXIII, Heft 2, 1899, Cap. I en II. This is the reason that never any experiment can be performed concerning the germination of this pollen in any liquid without having first examined, — by control experiments, by preference with the pollen from the same anther, — whether it passes into germination in destilled water, either or not. If this precaution is neglected there is great risk to

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draw a wrong conclusion from the germination experiments. The pollen of this *Begonia*, for instance, I have repeatedly seen germinating in solutions of saccharose, dextrose and mannite of different degrees of concentration, but as often the same experiment did not succeed. Now one might be inclined herefrom to conclude, that in this species of pollen germination can be stirred by the said sugars; but this is by no means the case: to the solutions mentioned this pollen is perfectly indifferent. The divergent results are explained in this way, that the said pollen at one time germinates in water, at another time not. If it does *not* germinate in water the process cannot be called forth by saccharose, dextrose, mannite or asparagine, if it *does*, this also takes place in solutions of these substances, and so, this is to be taken in such a sense that saccharose, dextrose and mannite have not the power of preventing the germination.

In presence of a stigma of the own plant it invariably germinates and likewise if the liquid contains a trace of levulose, indifferently whether the levulose is added to the destilled water, or to a solution of saccharose, dextrose, mannite or asparagine.

The three other species of *Begonia*, *B. semperflorens*, *B. Deppii* and *B. imperialis*, behave towards water, dilute stigma-liquid, and kinds of sugar, in the same way as the pollen of *Mussaenda*, i. e. do not germinate in water, but only in dilute stigma-liquid and in liquids containing levulose.

Now it is certainly striking that levulose acts quite differently on the pollen of the *Pavettas*. Of some of these, namely of *P. macrothyrsa* and *P. Reginae*, the pollen germinates already in destilled water; that of *P. javanica*, *P. fulgens*, *P. longipes*, *P. pauciflora*, *P. grandiflora*, and others, only in presence of a stigma.

For all these *Pavetta*-species however, the presence of levulose is an obstacle to the development of the pollen-tube. Of not a single species I have been able to make the pollen germinate in levulose, and what in particular deserves attention, is that of most *Pavettas* the germination is not only prevented, but that the pollen bursts and allows its contents to stream out when brought into contact with a liquid containing levulose.

What has just now been communicated about the relation of the pollen of *Begonia gorgocensis* to water, holds also good for that of *Pavetta macrothyrsa*.

Now it forms beautiful tubes in this liquid, then again no trace of germination is to be detected. In the latter case the process of germination is not to be called forth by saccharose or dextrose, whilst, if it does germinate in water, addition of these sugars does

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impede the process. If now to the liquid a trace of levulose is added, whether this liquid consists in destilled water or in a solution of sugar, the coats burst and the contents spread in the liquid.

I have not succeeded in finding a chemical compound able to call forth germination in *Pavetta*. What has been told above about the different behaviour of this pollen towards the stigma-liquid of the plant itself and towards that of other species, makes it appear probable that in distinct species there are also distinct substances present in the stigma-liquid. Which substances however these are, I have not as yet been able to detect.

The pollen of *Murraya exotica* (belonging to the *Rutaceae*) corresponds in its relation to levulose completely with that of many *Pavettas*. Put in water, the pollen-grains show a commencement of germination. As a rule the tubes attain no greater length than of 1—2 times the diameter of the pollen-grains. In dilute stigma-liquid or in a solution of saccharose, mannite or dextrose, the growth of the tubes is not furthered. In this solution the pollen behaves as in water.

On addition of levulose, however, whether to the water, or to the sugar solutions, the grains burst and there is no question of formation of tubes.

What has been said here about the prejudicial action of levulose on the pollen of *Murraya exotica*, has induced me to examine whether this pollen might be caused to germinate in the dilute stigma-liquid of *Mussaenda*. If the pollen of *Murraya* would burst in a liquid wherein a stigma of *Mussaenda* is laid, then the supposition that the chemical compound which in the stigma-liquid of *Mussaenda* causes germination, is levulose, would have acquired a high degree of probability.

It has now become evident to me that this is not the case; the pollen of *Murraya* does not die in the dilute stigma-liquid of *Mussaenda rufinervis*; it germinates in it in the same way as in water.

The possibility is not excluded that still we have to do here with levulose, but that this compound, diffunding from the stigma-liquid produces a too weak solution to act prejudicially on the pollen of *Murraya*; but how this may be, the said experiment shows that the substance able to cause germination in the stigma-liquid of *Mussaenda*, cannot, as yet, be identified with levulose.

The fact that the pollen of some *Pavettas* is greatly prejudiced by levulose, while that of other *Pavettas* and of *Murraya exotica* is even destroyed by the presence of that substance in the germin-

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ation liquid, has induced me, also for a few other plants, to examine how their pollen behaves towards levulose, of which research the results follow here:

The pollen of *Ipomoea imperialis*, *Calonyction speciosum (Ipomoea bona nox)*, and of some other cultivated species of *Canna*, belong to those species of pollen which are not proof against water.

The grains burst immediately after they have come into contact with water and the same takes place in dilute solutions of saccharose. Only at a concentration of 20 pCt. no rupture of the pollen-coats occurs; it remains intact, but does not pass into germination.

If now, however, to such a solution a trace of levulose is added, the grains burst just as in water.

The pollen of a species of *Acanthacea*: *Justicia (Tyloglossa)* cultivated at Batavia and Buitenzorg, is perfectly proof against water and sugar solutions. It can remain in it for a long time without any change being observed and without passing into germination.

A slight quantity of levulose, however added to the destilled water, or to the saccharose solution, causes the pollen to burst.

Of *Antirrhinum* spec. [*Maurandia antirrhinifolia* Hort. Bog.] the pollen germinates in water; a solution of saccharose does not impede the germination, so long as the degree of concentration does not exceed 5 pCt. Addition of levulose prevents the germination, the pollen-grains, however, do not burst.

The pollen of *Pentas carnea*, of which the germination in water is doubtful (like that of *Begonia gorgocensis* and *Pavetta macrothyrsa*) germinates, on the contrary, with very fine tubes in presence of levulose, whilst, lastly, the pollen of *Impatiens Sultani* and *Impatiens latifolia*, which germinate in water, are as little prejudiced by levulose as by saccharose and dextrose.

It will be remembered that STRASBURGER [1]) has come to another conclusion.

From his observations, that pollen could often come to germination on stigmas of plants having no systematic affinity to the specimen which produced the pollen, and that the pollen-tubes of foreign pollen, could often penetrate through the canal of the style, a little way into the ovary, STRASBURGER thought himself justified in inferring that no preventives occurred on the stigma against the germination of foreign pollen.

He was therefore of opinion, that when a foreign pollen species does not germinate on a stigma this should not be considered as a favorable adaptation, but much more as an accidental phenomenon

[1]) STRASBURGER. Ueber fremdartige Bestäubung, PRINGSHEIM's Jahrb. Bd. XVII, 1886.

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caused by this pollen being exposed on that stigma to prejudicial influences, or by its not finding there the conditions of nutrition required for the development of the pollen-tube.

That foreign pollen-tubes get only rarely into the ovary and still more rarely between the ovules, would further be related to the circumstance that the noxious influences to which they are exposed in the extraordinary surrounding accumulate more and more, and so the conditions become still more unfavorable.

Protecting contrivances against foreign pollen would in consequence not exist, and it was STRASBURGER's opinion that they were superfluous because the investigation had taught him, that the normal development of the plant's own pollen was not prevented by the presence of foreign pollen.

The tubes of the own pollen grew unhindered among the foreign tubes and arrived to normal function.

It seems to me that STRASBURGER's observations are not sufficient to prove that no protecting contrivances are found against foreign pollen.

Opposite to the fact that pollen of the most distinct botanic origin can come into germination on a determined stigma, is the fact that still a great many other species of pollen cannot be stimulated into the formation of pollen-tubes on it at all, and this holds good even for pollen of plants which stand in close, even in the very closest affinity to the stigma-bearing specimen.

This latter fact, as it will appear to me, points as clearly to the existence of protective means, as the reverse points to the opposite.

Besides, when the tube of foreign pollen together with the own pollen, penetrates a little way into the style-canal, but then ceases growing, while that of the plant's own pollen goes on and reaches the ovule, this is not necessarily the consequence of an accumulation of unfavorable influences.

It is not impossible, and even not improbable, that the further growth of the pollen-tube and the penetrating into the micropyle is bound to special exigencies satisfied only for the plant's own, or for allied pollen. Those special exigencies for further growth may be obtained by adaptation.

I think that from STRASBURGER's research no more must be deduced, than that *not always* preventive means are found on the *stigma* against fertilisation with foreign pollen. Doubtful it is, moreover, whether it is really relations of nutrition, which govern the germination on the stigma and the penetrating of the tubes into the style-canal.

The fact that many species of pollen require a determined degree

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of concentration in a sugar solution in order to germinate, and cannot be brought to the formation of the tube above and below that degree, points, as it seems to me, to quite other relations than those of nutrition, while the fact that number of pollen species form beautiful and long tubes in destilled water, proves that in any case not all species of pollen must find on the stigma a nutriment specially fit for their growth.

There are number of facts which decidedly point out, that for some plants there exist really preventives on the stigma against fecundation with a particular kind of pollen. STRASBURGER calls them exceptions, but still they are so striking as to highly draw the attention.

So it is already known since DARWIN, that the long-styled form of *Linum grandiflorum*, a heterostyle-dimorph plant, is absolutely sterile when fertilised with the illegitimate pollen of the same species, and this is likewise the case with the illegetimate pollen of both forms of *L. perenne*. Nobody doubts but the sterility of these both plants when fertilised with illegitimate pollen should be considered as an adaptation.

With *Linum grandiflorum* the pollen-grains donot try at all on the stigma to form tubes.

With *Linum perenne* they do, but the pollen-tubes do not reach the ovary, or at least are not able to fecundate the ovules. Would it not be allowed to conclude therefrom, that both species have the means to protect them against illegitimate fecundation, that these means for *Linum grandiflorum* are already found on the stigma and for *Linum perenne* in the style-canal?

The pollen of *Oncidium flexuosum*, *O. unicorne*, *O. pubes* and of some other *Orchideae* [1]) is not only unable to fertilise its own flower, but it has even a poisonous effect on the stigma. Here again the preventive against self-fertilisation is found on the stigma. In *Corydalis cava*, on the other hand, whose own pollen germinates very well on the stigma, but where the tubes do not reach the ovules, it is evidently found in the ovary, etc.

If now in these cases there is nothing else to be thought of but a special contrivance, then it might a priori also be expected that preventives should be found against fecundation with foreign pollen *in general*, and that they should be sought in the first place on the stigma, and if not found there, in the style-canal and the ovary. To this view I think to have given some support in the above communication.

Batavia, May 1900.

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[1]) DARWIN, Variation etc, Chapter XVII.

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Physics. — Communication N°. 59[a] from the Physical Laboratory by Prof. H. KAMERLINGH ONNES: "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface. I. Graphical treatment of the transverse-plait*".

(Read June 30, 1900.)

1. According to VAN DER WAALS' theory it is possible by means of a sufficient number of well selected observations with mixtures of two known normal substances, to determine the constants (a_{12} and b_{12} of VAN DER WAALS), which allow us to construct the general equation of state for the mixtures of these substances and especially to predict the phenomena of condensation by ψ-surfaces derived from that equation of state.

KUENEN, who among other things aimed at determining VAN DER WAALS' constants for mixtures of methyl chloride and carbon dioxide, has mentioned already in his thesis for the doctorate that calculations had been made in order to construct the ψ-surfaces from the observations for mixtures of these substances.

I have carried out and very nearly completed these calculations for the temperature at which KUENEN has made his most important observations, i. e. those on the retrograde condensation.

For each of the values of the molecular proportion of CO_2 in his mixtures $x = 0$, $x = 1/4$, $x = 1/2$, $x = 3/4$, $x = 1$ KUENEN gives the values of the constants R_x, b_x, β_x, $K_x = Ta_x$ in the equation of state

$$p = \frac{R_x T}{v - b_x} - \frac{K_x}{T(v + \beta_x)^2}$$

(p = the pressure in atmospheres, v = the volume referred to the normal-volume, T = absolute temperature).

By means of this I calculated the free energy for mixtures of the composition x,

$$\psi_x = -\int p\, dv + R\, T \left\{ x \log x + (1-x) \log (1-x) \right\},$$

(to which [1]) a temperature function linear in x can be added [2])) for equal

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[1]) In the drawings we have used for $\int p\, dv$: $\int_{\infty}^{v} p\, dv + 9.4383$.

[2]) VAN DER WAALS. Théor. Moléc. p. 11.

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molecular quantities and then represented them graphically (see Pl. II, fig. 2); the abscissae represent 100,000th parts of the theoretical normal volume, and the ordinates give — ψ_x in atmospheres $\times$ the theoretical normal volume, so that these lines are projections on the $x\psi$-plane of sections of the ψ-surface by planes $x = 0$, $x = 1/4$, $x = 1/2$, $x = 3/4$, $x = 1$. The x-coordinate is chosen perpendicular to the ψv-plane as in the case of VAN DER WAALS. For the mixtures $x = 3/8$ and $x = 5/8$ values of a_x, b_x, β_x, R_x were chosen as nearly as possible in agreement with those given by KUENEN and ψ-lines were calculated with these also.

We then derived from these lines the projections on the $x\psi$-plane of the sections of the ψ-surface by planes $v = \text{const.}$, which are represented in Pl. II, fig. 1 and other auxiliary lines were drawn, which lines together with their projections on the xv-plane, shown in fig. 3 and 4, will be considered in the following §§.

In this way we succeeded in obtaining by means of the constants a_x and b_x derived from the observations a representation of the entire first plait in the case of KUENEN's experiments.

Originally however I expected to attain more in a graphical manner. For the condensation phenomena can be easily followed in all their details when the binodal curve and the direction of the tangent-chords are known (comp. following communication § 5), whereas the determination both of the binodal curve and the tangent-chords themselves from the equation of state by analytical processes is certainly exceedingly complicated even when it is feasible.

I had hoped that this problem of VAN DER WAALS' theory could be graphically solved using as a basis the graphical representation mentioned and that it would have enabled me to determine numerically all the phenomena of condensation from the knowledge of a small number of constants (VAN DER WAALS' a_{12} and b_{12}, if necessary augmented by some empirical constants of correction) in the way mentioned in the beginning of this paper for any mixture at any temperature. But this proved to involve great difficulties.

2. The difficulties which hinder us from obtaining an exact numerical solution, proceed from the fact that VAN DER WAALS' theoretical equation of state both as originally given and as modified empirically by KUENEN according to CLAUSIUS, do not give with sufficient accuracy the real behaviour of the pure substances and the mixtures.

We tried whether from isothermals, experimentally determined by KUENEN at higher temperatures combined with RAMSAY's simple

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relation for the variation of the pressure with the temperature $p = AT + B$, the isothermals in the unstable part could be extrapolated. But this did not lead to a satisfactory result.

Therefore it is absolutely necessary to use an equation of state in sufficient agreement with the observations, however empirical its form may be, in order to foretell from other observations on mixtures of two substances the phenomena of condensation of mixtures of those same substances under definite circumstances.

In the equation of state used by KUENEN we have allowed for the fact that a_{11} and a_{22} are temperature functions as has been also assumed by VAN DER WAALS for other developments. The identity used by KUENEN $Ta_x = K_x$ where $K_x = K_{11}x^2 + 2K_{12}x(1-x) + K_{22}(1-x)^2$ causes the replacement of a_{12}, which probably is also a temperature function, by the less variable K_{12}, but this K_{12} cannot, any more than a_{12} be determined with sufficient accuracy from the observations.

As for the empirical correction by means of CLAUSIUS' β, we cannot accept that this would lead us to the calculation of the pressure of the mixtures with a definite composition, volume and temperature, at any rate not to the calculation of the pressure in conditions such as that of the co-existing phases, with an accuracy within the limits of the errors of observation. For it is only within a limited range that this empirical correction holds in the case of a simple substance. Much more is to be expected in this direction from the rational method for the determination of empirical corrections of VAN DER WAALS' a and b, followed by REINGANUM in his thesis for the doctorate [1]).

In order to obtain, regardless of any equation of state, empirically true representations of observed isothermals, I have tried to represent these accurately by means of a series within the limits of the errors of observation. The investigation relating to this, has been progressing, so that I hope to be soon able to give a communication on this subject. The following however has been worked out independently of the results obtained thereby.

Even if one has at one's disposal a sufficiently accurate series or other empirical representation for one simple normal substance, from which might be calculated that for a second similar substance [2]) (i. e. belonging to the same class of substances) according to VAN DER WAALS' law of corresponding states by means of two constant relations (for instance that of the critical pressures and that of the critical

[1]) M. REINGANUM, Theorie u. Aufstell. einer Zustandsgleichung. Diss. Göttingen 1899.

[2]) KAMERLINGH ONNES, Verh. Kon. A. v. W. Amsterdam 1881, p. 11.

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temperatures) even then the question remains how far the homogeneous mixtures of two similar normal substances satisfy the law of corresponding states. At present it is doubtful whether this is the case in the same degree as for simple substances of the same group, as a mixture is generally not mechanically similar to a simple substance [1]). According to VAN DER WAALS' law however the homogeneous mixtures satisfy his law of corresponding states. Therefore we may call this theory, the theory of the *ideal mixture*. According to that theory we can calculate the isothermal for each mixture from that of a simple standard substance by means of 2 constant relations, e.g. those of the critical temperatures T_{xk} and critical pressures p_{xk} of mixtures of the composition x, provided they are homogeneous; or expressed differently: the ψ-curve can be obtained from that of the simple substance by linear magnification in two directions [2]). As a given ψ-surface corresponds to a given T, the ψ_x-lines appearing on it (given by

$$\psi_x = -\int p dv + RT\left\{x \log x + (1-x)\log(1-x)\right\}$$

$$\Psi_x = \frac{\psi_x}{Cp_x v_k} = \frac{\psi_x}{RT_{kx}} = -\int \frac{p\,dv}{Cp_k v_k} + \frac{T}{T_{kx}}\left\{x \log x + (1-x)\log(1-x)\right\}$$

$$\Psi_x = \frac{\psi_x}{RT_{kx}} = -\frac{1}{C}\int \pi\, d\omega + \tau_x\left\{x \log x + (1-x)\log(1-x)\right\},$$

where π and ω are the reduced pressure and the reduced volume, Ψ_x the reduced ψ_x and C a constant identical for all substances of the same group [3])), can be derived from the ψ-curves for a simple similar substance, but they relate to the reduced temperatures $\tau_x = \frac{T}{T_{xk}}$ [4]).

In how far mixtures of normal substances deviate from this ideal case has not yet been investigated, to solve this problem it will

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[1]) Comp. ibid. p. 24.

[2]) Comp. ibid. p. 23.

[3]) Comp. ibid. § 4.

[4]) The conditions for thermodynamical similarity have been given by me in Comm. n°. 23. Zittingsverslag 25 Jan. '96. Only when these conditions are satisfied, the temperature function which is linear in x will vary in a corresponding manner for the different temperatures.

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be necessary to make observations, not less extensive than those by AMAGAT for simple substances.

If we accept that the mixtures obey the law of corresponding states, we must yet consider how far we may express the critical temperatures, pressures (and volumes) for such mixtures by means of two constants a_{12} and b_{12} by the equations

$$T_{xk} = C_1 \frac{a_{11}\,x^2 + 2\,a_{12}\,x\,(1-x) + a_{22}\,(1-x)^2}{b_{11}\,x^2 + 2\,b_{12}\,x\,(1-x) + b_{22}\,(1-x)^2}$$

$$p_{xk} = C_2 \frac{a_{11}\,x^2 + 2\,a_{12}\,x\,(1-x) + a_{22}\,(1-x)^2}{\{b_{11}\,x^2 + 2\,b_{12}\,x\,(1-x) + b_{22}\,(1-x^2)\}^2}$$

$$v_{xk} = C_3\,\{b_{11}\,x^2 + 2\,b_{12}\,x\,(1-x) + b_{22}\,(1-x)^2\}$$

in which C_1, C_2 and C_3 are the same constants for all substances, or whether more complex functions of x are required therefor.

For the treatment of these two last problems in the case of KUENEN's experiments I refer to a joint communication by Dr. M. REINGANUM and myself [1]).

With reference to KUENEN's experiments, it may be mentioned that a new reduction of the combined observations (by means of graphical representations and by series) is being worked out, from which we can deduce more satisfactorily than is now possible what degree of accuracy is attained in these experiments.

3. Now I return to the treatment of the problem to be solved.

I have made use for this purpose of two methods, and have sometimes completed the results of the one with those of the other method.

In the first place, from the drawings mentioned in § 1, other graphical representations are deduced by means of constructions, which lead to the solution of the problem in hand, (comp. for instance § 8); this will be called *the graphical method in a plane.* In the second place, a plaster cast of VAN DER WAALS' surface was made [2]) in order to make constructions on it, for instance to determine the connodal curve by rolling a glass-plate covered with lamp black over the plait. This will be called *the graphical method by the model.* With the first method, when the equation of state $p = f\,(v,\ x,\ T)$ has once been given, the accuracy can be raised indefinitely without any material difficulties. The only thing

[1]) Same Proceedings, following paper.

[2]) A diagrammatical model of the ψ surface has been made by VAN DER WAALS and is represented in Théor. Mol. p. 28.

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necessary is to make new drawings on a larger scale relating to those parts of the surface that are to be investigated more in detail (comp. 59^b).

With the second method the material difficulties increase, whether we desire to make casts of greater dimensions, or to add separate detailed casts on a larger scale as auxiliary figures to the original casts, as soon as we wish to attain a higher degree of accuracy (comp. 59^b). This becomes obvious when we see how little defined are the plaits by which the phenomena of condensation are determined, especially in the neighbourhood of the plait-point which strikes one immediately when one compares Pl. I.

For my first treatment of KUENEN's experiments I used only the graphical method in a plane. But as the numerical treatment of the problem became more difficult, the value of the qualitative treatment increased.

As soon as I could avail myself of the assistance of a modeller, Mr. ZAALBERG VAN ZELST, I had a plaster-cast of the ψ-surface made from the graphical representation in plane. For this purpose moulds were used constructed from curves calculated and drawn by me for $\psi_x = f(v)$ and $\psi_y = f(x)$ (comp. § 1).

When the cast — 30 cm. long, 20 cm. wide and 40 cm. high — was ready, though able to give a distinct representation of the plait, it appeared too small for several constructions and so a new cast was made of twice these dimensions, based on the same drawings. This larger pattern, even when hollowed, is rather heavy (80 K.G.) but it proved to be highly satisfactory for several constructions. By rolling the glass plate over it, a fairly regular binodal line with the tangent-chords was obtained, and so the relative positions of the critical point of contact and of the plaitpoint could be demonstrated. For the construction of the curves $\frac{d\psi}{dv} = p = \text{const.}$, the curves of pressure, and $\frac{d\psi}{dx} = \text{const.}$, the curves of substitution potential, (obtained in the graphical representation in plane by drawing lines of contact), a hinged pair of bars with level and scale was used (see fig. 1), which is placed on the cast by means of two pins separated by one cm. The curves drawn on the cast can be easily projected by means of a system of curves $v = \text{const.}$ and $x = \text{const.}$ The tangent-chords to the cast were represented by stiff wires.

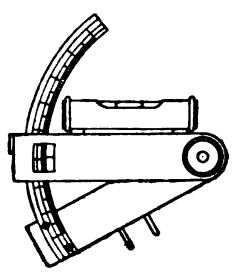

Fig. 1.

The cast thus obtained was in the main the

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same as that represented photographically on Plate I. Among other things fig. 5 Plate I in HARTMAN's thesis for the doctorate was derived from it [1]). Photographs of this surface were given by me to some colleagues at the Naturforscherversammlung at Dusseldorf (1898), also I presented a few persons interested in it with casts of the smaller pattern and of that part of the larger pattern which is near the plaitpoint.

4. If at the time, the construction of a model to accurately represent the reality involved many difficulties resulting from the complications mentioned in § 2, it appeared to me, as the number of the applications of VAN DER WAALS' theory increased, to become more and more desirable to know in detail the properties of the plait obtained, especially in the neighbourhood of the plaitpoint, and to render the graphical construction of the connodal line, the tangent-chords and the condensation phenomena now more useful rather for explaining this theory than for calculating the numerical results of the observations from VAN DER WAALS' theory. For it is obvious that a true knowledge of the behaviour of ideal mixtures is an indispensable guide in experimental researches of real mixtures. And the difference will not be so very important if we allow the ψ-curves in this illustration to deviate as they approach the side of the small volumes, provided that this is done in a corresponding manner. I resolved therefore to modify the cast in order to make it suit the desired purpose.

For this care must be taken, that at any rate the ψ-curves assumed for the simple substances strictly satisfy the law of corresponding states. But on the other hand, the desire to illustrate VAN DER WAALS' theory for a case, which agrees as well as possible with actual measurements — in this case KUENEN's — remained justified. Therefore it seemed to me desirable to apply the empirical correction, obtained by including CLAUSIUS' β_x into the equation of state, which also analytically only slightly changes most of the developments of VAN DER WAALS. Here the β_x must satisfy the condition that $\frac{\beta_x}{b_x} = n$ for all mixtures has the same value as for the two mixed substances.

For a given ψ-surface, it is of no moment that we put $Ta_x = K_x$, yet this supposition has been included in VAN DER WAALS' equation of state in order to link the latter to the observed isothermals

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[1]) CH. M. A. HARTMAN, Metingen omtrent de dwarsplooi op het ψ-vlak van VAN DER WAALS bij mengsels van chloormethyl en koolzuur. Diss. Leiden 1899.

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for other temperatures and to better deduce the critical temperatures and the critical pressures of the homogeneous mixtures T_{xk}, p_{xk}.

(The two above mentioned empirical corrections used by CLAUSIUS were chiefly employed to obtain a better agreement with the density and the tension of the saturated vapour. And so it is obviously useful to apply them where we have especially in view the phenomena of condensation.)

For K_x and b_x we kept to the (ideal) form of the second degree in x of VAN DER WAALS.

For these reasons we chose as the equation of state

$$p = \frac{R\,T}{v - b_x} - \frac{K_x}{T(v+\beta)^2}$$

$$K_x = K_{11}\,x^2 + 2\,K_{12}\,x\,(1-x) + K_{22}\,(1-x)^2$$
$$b_x = b_{11}\,x^2 + 2\,b_{12}\,x\,(1-x) + b_{22}\,(1-x)^2$$

$$\beta = n\,b$$

v expressed in terms of the theoretical normal volume.

The reasons for choosing the new values for a_{11}, a_{22}, a_{12}, b_{11}, b_{12}, b_{22} and for $n = \frac{\beta}{b}$, are explained in a combined communication with Dr. REINGANUM, who to my great satisfaction I found ready to undertake together with me the accurate graphical investigation of that part of the surface near the plait-point which on fig. 3, Pl. II is shown by the small rectangle. The original cast was modified in connection with that combined investigation until it agreed with the new data. I owe thanks for the valuable assistance of Dr. REINGANUM in this and in the following constructions.

5. Plate I shows a photographical reproduction of the cast obtained in this way, taken from the side corresponding to the methylchloride. The ψ-curve of pure methylchloride stands out clearly by the shadow and has moreover been dotted. The depth in the plait is revealed by the shadow cast by the tangent-chords. The representation of the casts did not appear to be so much improved by stereoscopic photographs, that it outweighed the greater complication of the process.

Fig. 1, 2 and 3 of Pl. II are the above mentioned projections on the ψx ψv, and xv planes of curves drawn on the ψ-surface. [1]) In fig. 1

[1]) In order not to render the drawings indistinct we have not drawn a rectangular system of equidistant lines a thing which can easily be done by every one who wants to make numerical readings on the drawings.

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(projection on the $x\psi$-plane) the projections of the substitution potential curves, or more simply the *substitution curves*, $\left(\frac{d\psi}{dx} = \text{const.}\right)$ have been dotted. In fig. 3 (projection on the xv-plane) the *pressure curves* $\left(-\frac{d\psi}{dv} = p = \text{const.}\right)$, are drawn, and the substitution curves are dotted. In fig. 4 the substitution curves are dotted and the curves for which $\psi + \frac{d\psi}{dx}(1-x) - \frac{d\psi}{dv}\, v = \mu_2 = \text{const.}$, the *potential curves* of the second component, are lined. According to VAN DER WAALS' theory (Théor. Moléc.) these three curves are sufficient for the determination of the co-existing phases.

How the substitution- and the pressure-curves have been obtained is mentioned in § 3. The graphical determination on the cast was tested with that on the plane.

6. First must be mentioned briefly how the potential curves are determined, both by construction on the plane and on the cast. In the first case I started from the figures 1 and 2, Pl. II, which give the sections of the ψ-surface by planes containing the line $v=0$, $x=1{,}000$ (the ψ-axis on the side of the methylchloride). If in fig. 2 we rotate [1]) the xv-plane with the lines $x = \text{const.} = A, x = B$ etc., (the projections of the ψ_x-curves) drawn on it, round the v-axis on the ψv-plane, the plane of the figure; the sections a, b etc. of the planes just mentioned, containing the line $x=1{,}000$, $v=0$, by the xv-plane, rotate into the plane of the figure and appear as radii (starting) from the point $x = 1.000, v = 0$, whose points of intersection aA, aB with the rotated lines $x = A, x=B$ etc. give the value of v for the point of intersection aA, aB, etc. of the plane a with the curves ψ_A, ψ_B etc. The line drawn in Pl. II fig. 2 through the point of intersection perpendicularly to the v-axis determines through the intersection aA with the ψ_A-curve the value of the perpendicular height above the v-axis, for the point aA' in the rotated figure; while the value of v for this point in the rotated figure is found by rotating the radius drawn from $x = 1{,}000$ $v = 0$ to Aa on the v-axis. The points aA', aB' etc. combined give the rotated oblique section a'. From one point μ_2 on the ψ-axis (line $x = 1{,}000, v = 0$ for the ψ-surface, $v = 0$ for the plane fig. 2) tangents are drawn to these rotated oblique sections a', b', whose points of contact

[1]) The drawing with these constructions can be omitted as it is somewhat complicated.

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$\mu_{a'}$, $\mu_{b'}$, $\mu_{c'}$ are points of contact of a plane drawn through the point μ_2, with the ψ-surface, which points of contact $\mu_{a'}$ $\mu_{b'}$ etc. are rotated on the plane of drawing round the line $x = 1{,}000$, $v = 0$. The co-ordinate $\psi_{\mu a'}$ of $\mu_{a'}$ in the drawing is also the co-ordinate $\psi_{\mu a}$, of the point of contact in the section with the plane a, returned into its previous position, while the abscissa $v_{\mu a}$, measured along the radius a gives the place of the projection on the xv-plane of the point of contact μ_a. The points μ_b, μ_b . . . are therefore combined by a smooth line into a potential curve for the value μ_2. The different curves, obtained by repeating the last constructions with several values of μ, give the system of potential curves in the xv-plane, fig. 4, Pl. II when the v-axis of fig. 2 is again considered as v-axis and the ψ-axis of fig. 2 as x-axis.

The construction by means of the model is immediately derived from this. We used a pair of sliding compasses with points, long enough to continue the construction also within the plait. One of the points has the ordinary form, and is placed on the top of a rod which is movable in the line $x=1{,}000$ $v=0$ and terminating at the height μ. The other movable point is fork-shaped (see fig. 2) of which the two prongs one cm. apart are situated in a straight line with the fixed point. When, during the sliding of the fork, we try where the two teeth rest on the cast, we find the place where a line of contact to the surface, goes through the point μ. In order to obtain the projection of the potential curve found on the cast, we use again the system formed by the curves $v = \text{const.}$ $x = \text{const.}$ on the ψ-surface.

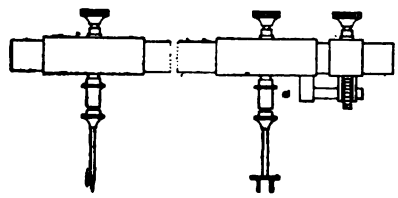

Fig. 2.

7. The figures drawn seem to me well adapted for giving us a very clear representation of the thermodynamical properties of the mixtures according to VAN DER WAALS' theory.

Many peculiarities are to be observed in the course of the different lines. I shall draw attention to only a few. The limiting-forms of the pressure-curves are for very large volumes straight lines across the surface, parallel to the x-axis; with small volumes the curve tends again to become rectilinear, but in that case its general direction is at some small angle with regard to the x-axis. This follows immediately from the theory. The point of inflection of the pressure-curves through the plaitpoint is situated, reckoned from the liquid-side, farther than the plaitpoint (this property was formerly

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communicated orally to me by VAN DER WAALS). Through both the ends of a tangent-chord pass the same curves of pressure, of substitution and of potential (a thing which we can see for ourselves by laying the tracing of one figure on the other). Through these points pass also the potential lines for the first component. These are the chief conditions advanced by VAN DER WAALS.

The curve of pressure touches the tangent-chord in the critical point of contact. This has been pointed out by HARTMAN (Comm. N°. 56).

The points of intersection of the theoretical and the experimental isothermals are situated almost in a straight line going through the critical point of contact. The point of inflection of the pressure curves in the unstable part is situated also in a line deviating but slightly from a straight line towards the side of the small volumes; the critical point of the homogeneous mixture lies also towards the side of the small volumes, with regard to the point of intersection with the experimental isothermal. (Comp. HARTMAN, footnote Comm. N°. 56).

The substitution curves run parallel to the v-axis for large volumes. For smaller volumes they begin to incline towards the plait, this inclination increases as they reach farther down into the plait, it attains a maximum and decreases again in the direction of the smaller values of x. The lowest point of the bend is outside the plait.

The substitution-curve of the plaitpoint envelops the connodal line, according to properties found by KORTEWEG, and shows a point of inflection that comes within the plait from the side of the smaller volumes. The substitution lines intersect the pressure curves within the connodal line. The divergence of their general direction in the plait agrees best with that of the tangent-chords.

The general direction of the potential lines for larger volumes lies obliquely over the ψ-surface from the side of the smaller volumes and smaller composition-ratios towards the side of the larger volumes and larger ratios. Towards the plait they show a bend, which is more acute than that of the substitution-line and on entering further into the plait these increase rapidly in acuteness, so that they, like the pressure curves project beyond the limits of the surface. The lowest point of the bend lies within the plait. The greatest convexity towards the plaitpoint of the substitution lines and of the potential lines coming from the side of the large volumes within the plait is situated together with the greatest concavity of the pressure-curves on that side more or less on the axis of the parobola by which

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the projection of the connodal-line is approximately represented (in other respects it is better represented by a hyperbola).

8. *The determination of the co-existing phases by graphical solution in the plane surface.* Attention has been drawn to the difficulties, attending the precise graphical solutions by means of the plaster-cast. These are very great when we want to determine the connodal-line by means of rolling a lampblacked glass plate over the cast, which method is in other respects the most direct expression of VAN DER WAALS' solution of the problem. Hardly perceptible deviations of the surface have a great influence on the shape of this curve. Therefore it is desirable to be able to determine the connodal-line and also the tangent-chords by a construction for which we only need to make drawings on a plane [1]). The graphical representations discussed in the former sections offer a means for this. For if we return to the condition advanced by VAN DER WAALS for the co-existence of two phases, namely

$$\left(\frac{d\psi}{dx}\right)' = \left(\frac{d\psi}{dx}\right)'', \quad \left(\frac{d\psi}{dv}\right)' = \left(\frac{d\psi}{dv}\right)'', \; \mu_2' = \mu_2'',$$

where ' refers to one phase and '' to the other, then we get to know the co-existing phases as those, in which μ_2 considered as a function of $\frac{d\psi}{dx}$ and $\frac{d\psi}{dv}$ for the same value of $\frac{d\psi}{dv}$ and $\frac{d\psi}{dx}$ twice has the same value.

If now we trace the course of a curve μ_2=const. in the curvilinear system of the pressure- and the substitution-lines in the xv projection, and if we transform this system of curves into one which is rectilinear and rectangular and on which along the axis of ordinates a suitable function of $\frac{d\psi}{dx}$ is measured, and along the axis of abscissae a suitable function of $\frac{d\psi}{dv}$, the μ-line by this process will become a loop-shaped figure, of which the double-point is at the values of $\frac{d\psi}{dv}$ and $\frac{d\psi}{dx}$, which correspond to the composition and the volume of the co-existing phases.

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[1]) RIECKE, Ueber die Zustandsgleichung von CLAUSIUS. Wied. Ann. 54, p. 739, treats the co-existing phases of a simple substance graphically) Comp. also H. K. O. Verh. Kon. Akad. v. Wet. XXII, p. 13, 1881), and mentions p. 744 that by means of the thermo-dynamical potential this could be done in a similar way for mixtures.

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For the representation of μ_2 as ordinate we have chosen in fig. 3

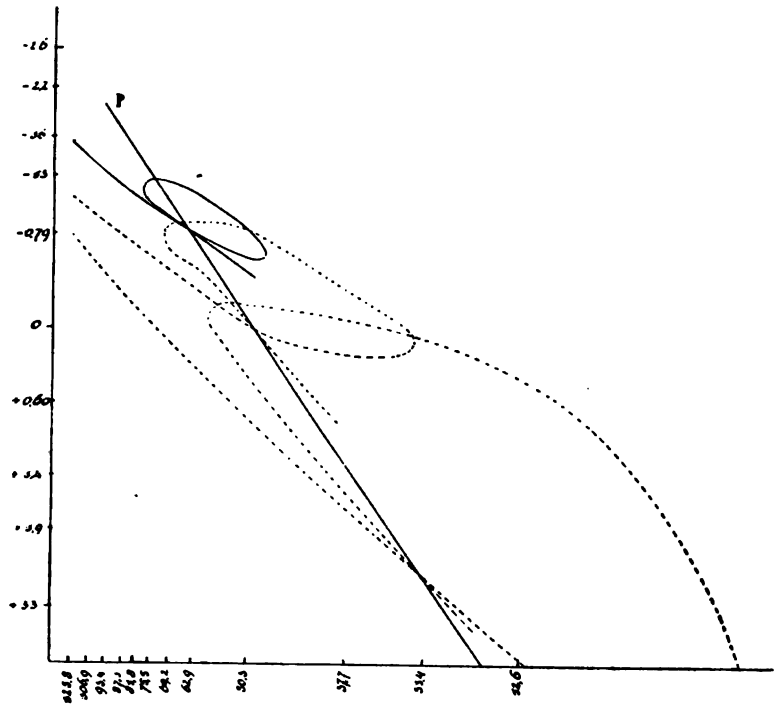

Fig. 3.

such a function of $\frac{d\psi}{dx}$, $s = f\left(\frac{d\psi}{dx}\right)$ that the substitution-lines, belonging to regularly increasing values of this s for large volumes, run at equal distances in the xv-plane. For simplicity's sake we have in order to determine s in this way not taken an infinitely large volume, for which we should have

$$s = \frac{e^{\frac{1}{RT}\frac{d\psi}{dx}}}{1 + e^{\frac{1}{RT}\frac{d\psi}{dx}}}$$

but the volume at the end of the drawing (0,034) fig. 3, Pl. I; where the value can be read directly. It does not deviate much from that for an infinitely large volume. As function of $\frac{d\psi}{dv}$ we might choose $w = \left(\frac{d\psi}{dv}\right)^{-1} = \frac{1}{p}$ so that for large volumes the pressure curves belonging to regularly increasing values of this w run at equal distances. But in order to be able to read the value immediately on the drawing fig. 3, Pl. II, we have chosen that function of p, which for $x = 0$ becomes equal to v.

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The shape of the closed loops in the annexed fig. 3, obtained in this way, still shows small irregularities, which are owing to inaccuracies in the construction. However I thought the figure of sufficient importance to give it here even in its imperfect state. Part of the loop-shaped figure for small proportions of the most volatile substance is in this case cut off by the curve $s = 0$. The line which connects the double points and therefore determines the pressure for co-existing phases as a function of the *substitution potential* $\frac{d\psi}{dx}$, is in this figure a straight line. As the substitution and the pressure-curves belonging to regular increasing values of w and s in the xv-plane for large volumes, form a nearly regular rectangular system, the connodal line in the xv-plane will also be a straight line for large values of the volumes. In connection with this result I may remark that according to an oral communication to me VAN DER WAALS has derived from his theory, that the connodal line for the plait into which the one investigated here passes at 9°,5 the temperature at which HARTMAN made his experiments, would be almost a straight line on the side of the large volumes, which is substantially verified by those experiments.

This appears from fig. 4 drawn by Dr. HARTMAN, in which the projections of the connodal line with the tangent-chords are represented for 9°.5. In order to make a comparison the plait on the model (almost that of KUENEN) has been added on the same scale as the drawing.

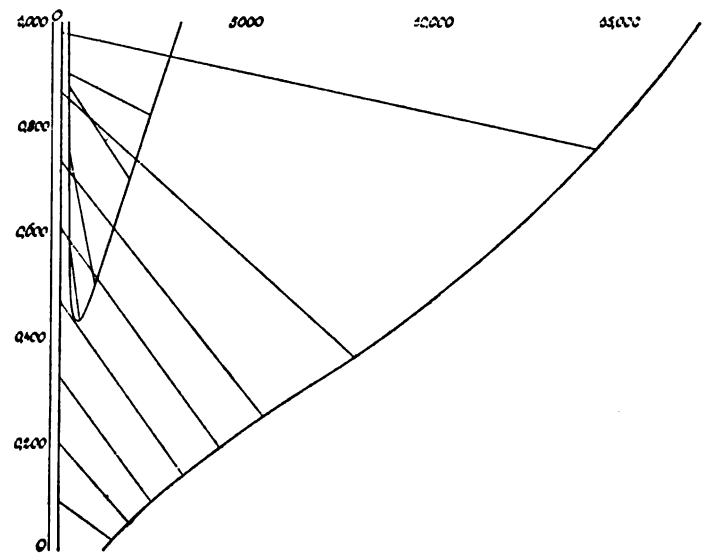

Fig. 4.

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Prof. **H. KAMERLINGH ONNES.** „**Contributions to the knowledge of VAN DER WAALS' ψ-surface. I. Graphical treatment of the transverse plait.**"

PLATE I.

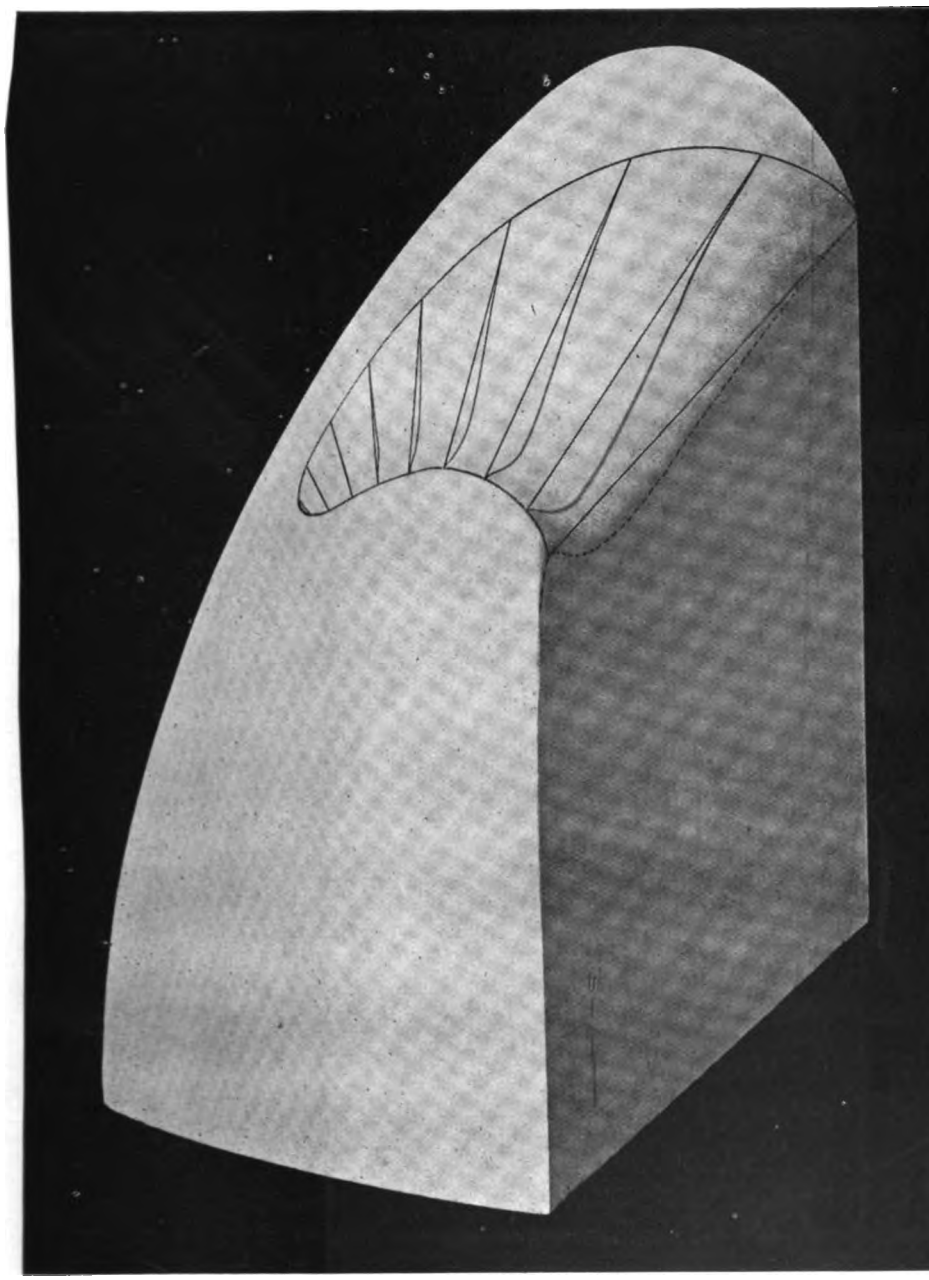

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PLATE II.

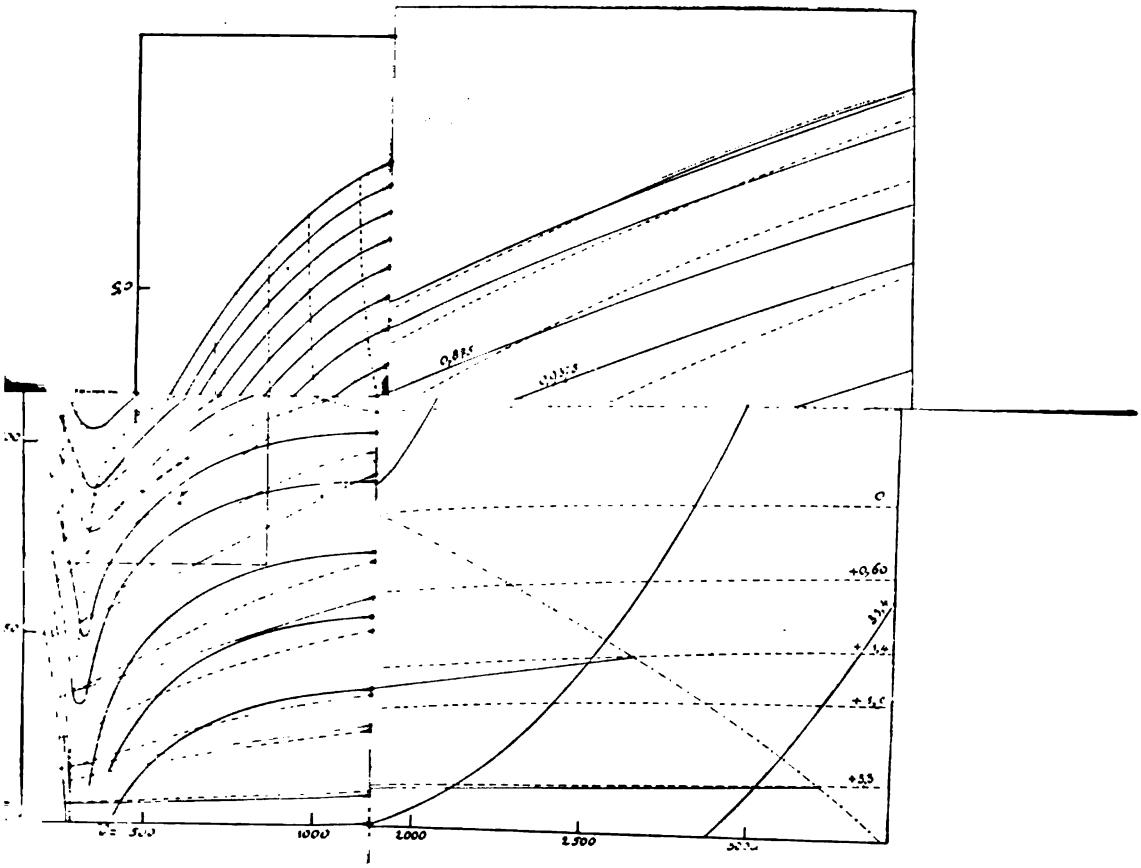

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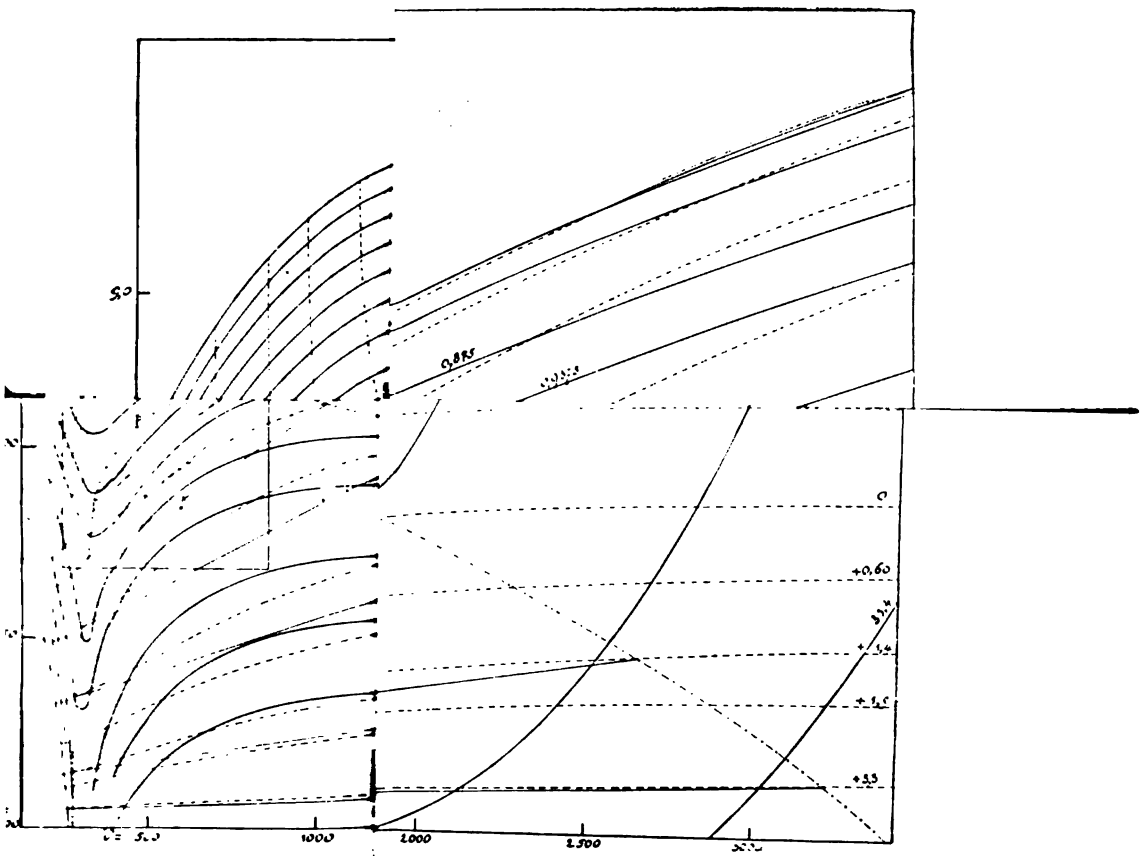
PLATE II.



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Physics. — Communication N°. 59^b from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES and Dr. M. REINGANUM: "*Contributions to the knowledge of* VAN DER WAALS' *ψ-surface*". II. "*The part of the transverse plait in the neighbourhood of the plaitpoint in* KUENEN's *experiments on retrograde condensation*".

(Read June 30, 1900.)

1. The most important part of a transverse plait in VAN DER WAALS' ψ-surface is no doubt that in the neighbourhood of the plaitpoint. For investigations of this part however a higher degree of accuracy is required than was sufficient for the construction of the model of the whole plait and of the constructions belonging to it, described in Communication N°. 59^a.

In the following pages we represent the part of the surface shown by a rectangle in figs. 3 and 4 of Pl. II, which representation is based on more accurate calculations of p (to 5 decimals) made for values of v and v in a smaller range by means of the same equation of state, from which we started for the construction of the general model. The principles on which the choice of this equation of state was based for the following illustration of VAN DER WAALS' theory have been laid down in § 4 of Comm. N°. 59^a; in the present paper we will consider the manner in which the constants occurring in that equation have been obtained, and in how far by this choice of constants the accepted equation of state can be made to harmonize with KUENEN's observations. As explained in § 2 Communication N°. 59^a two questions are specially prominent: 1st. in how far do the mixtures investigated by KUENEN agree with the law of corresponding states and 2nd. in how far can the critical constants of the homogeneous mixtures be represented by VAN DER WAALS' formulae of the second degree.

2. To obtain an opinion on this we cannot directly apply to KUENEN's observations the ordinary method of calculating the reduced values of the pressure, the volume and the temperature by means of the critical quantities. For the critical temperature of the homogeneous mixture (point K in fig. 3, Pl. IV) is situated according to VAN DER WAALS' theory in the unstable part and has therefore not been observed.

Neither are we assisted even to a moderate extent by RAVEAU's method of measuring off the logarithms of the pressure

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and the volumes as ordinates and abscissae and by then shifting the systems of isothermals of the two substances parallel to themselves until they cover one another. This is chiefly to be ascribed to the smallness of the range over which each of the isothermals extends. Those parts of the isothermals that can be drawn, show no striking curvatures and run almost parallel. Hence there is too much latitude in the adjustment, so that it is not possible to determine sharply enough the exact position in which the one system coincides with the other.

Therefore we can only very roughly consider the ratio of the absolute temperatures of two isothermals covering each other in the way mentioned, as being the ratio of the critical temperatures belonging to them; the same holds for the pressure and the volume.

It is obvious that we may use instead of the pressure itself, the product pv, which is moreover of so much importance for the investigation of the isothermals, draw for one temperature $log\, pv$ as a function of $log\, v$ and determine by shifting the curve $log\, pv = f(log\, v)$ on the one hand the ratios $\frac{p_{k1}v_{k1}}{p_{k2}v_{k2}}$ (or what comes to the same $\frac{T_{k1}}{T_{k2}}$) and on the other hand $log\, \frac{v_{k1}}{v_{k2}}$. As this still implies shifting the system in the direction of both the axes of co-ordinates, it also still offers too great a latitude.

We may do without the displacement in the direction of one of the axes, when we measure off not $log\, pv$ but $\frac{pv}{RT}$, which has the same value or molecular quantities in corresponding states. For large volumes this quantity has the value 1, for the critical state about 0.29.

In applying this method it appeared that it was not possible to completely cover the system of $\frac{pv}{RT}$ curves of the one substance by those of the other. Irregular deviations did show themselves, which may probably to a large extent be ascribed to errors of observation. The result was that a certain latitude still remained in the adjustments and the limits were sought within which the coincidence might be called satisfactory.

The ratio of the critical volumes follows immediately from the curves of $log\, v$ covering each other, which ratio could then only be included within the limits just mentioned.

The ratio of the critical temperatures is given by the temperature to which two $\frac{pv}{RT}$ curves belong, covering each other, so that this

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also can only be included within limits, while the same holds for the critical pressures, obtained by means of $Cp_k v_k = T_k$. For C we took the value found by AMAGAT for carbon dioxide.

The following table gives the results of these processes starting from $p_{k2} = 72.9$, $v_{k2} = 0{,}00426$, $T_{k2} = 304.35$ for carbon dioxide.

Proportion of CH_3Cl.	V_{kx}.	V_{kx}. mean.	T_{kx}	T_{kx}. mean.	p_{kx}.
$x = 1.0$	0.00668 to 0.00728	0.00698	413 to 419	416	63.2 to 57.8
$x = 0.75$	633 to 588	610	382 to 391	386.5	mean value 64.7
$x = 0.50$	654 to 675	665	337.5 to 340	339	mean value 52.2
$x = 0.25$	501 to 562	531	indefinite.	indefinite.	

For the critical temperature of pure methylchloride we find the same value as found experimentally by KUENEN (416.0). The mean value of the critical pressure (60.5) however deviates much (7,5 pCt.) from the value found by KUENEN (64.98). The highest value is in better agreement (3 pCt.)

We will naturally next consider how *the critical temperatures of the homogeneous mixtures* T_{xk} found by us, are situated with respect to *the critical point of contact temperatures* T_{xR} found by KUENEN.

This may be seen from the following table:

Mixture.	T_R	T_k
$x = 3/4$	396	386.5
$x = 1/2$	370.1	339
$x = 1/4$	338.4	indefinite

In good agreement with the theory, the values of T_k are found to be lower than those of T_R, and one would be inclined to fill in for $x = 1/4$, symmetrically with $x = 3/4$, $T_k = 328$. Yet the difference of 31° found for $x = 1/2$ gives rise to some objections against putting great trust in the determinations. If we also bear in mind the irregular deviations, remaining between the two systems covering each

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other, which leaves undecided whether the mixtures deviate from the law of corresponding states more than the simple substances, and also the large deviations found in determining the pressure of methylchloride, much uncertainty remains about the critical value itself.

Therefore it is desirable to try to deduce in a different way something about the critical temperatures and the pressures of the homogeneous mixtures from the whole of the observations for each mixture. We find a means for this in the equations given by KUENEN which express as well as possible the whole of the observations for each mixture, which equations we at first did not think it advisable to use in order that we should be as little biassed as possible in forming an opinion from the observations themselves about the problems in hand. But it is not to be expected that we can satisfactorily determine the critical quantities, firstly because KUENEN has not taken for all his mixtures the same temperature function for a, secondly as states situated far from the critical point, which have influenced the determination of the equations, can give rise to errors by the extrapolation with the defective equations of state.

However it may be considered as a confirmation of our conclusions from the adjustments when the former can also be derived from these equations.

With regard in the first place to the fulfillment of the law of corresponding states, we might conclude from the disagreement of the ratio $n_x = \frac{\beta_x}{b_x}$ given by KUENEN,

$x = 1$	$n_1 = 1{,}40$
$x = {}^3/_4$	$n_{3/4} = 1{,}26$
$x = {}^1/_2$	$n_{1/2} = 1{,}66$
$x = {}^1/_4$	$n_{1/4} = 1{,}38$
$x = 0$	$n_0 = 1{,}09$

that the mixtures investigated do not fulfill the law of corresponding states [1]). The value of this conclusion becomes smaller, when we consider that KUENEN has accepted b_x somewhat arbitrarily. Both this and the choice of different temperature functions for a must influence the values found for β, and although we may allow that the variation of the values of n indicates a peculiarity in the closely related quantities b and β, they can only support the conclusion but weakly, that the mixtures would satisfy the law of corresponding states to a smaller degree than the simple substances.

[1]) That n must have the same value for all substances that fulfill the law of corresponding states, has been demonstrated by KAMERLINGH ONNES, Verh. Kon. Akad. v. Wet. XXI, 1881, p. 20; Arch. Néerl. T. XXX, p. 112.

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Let us consider now what follows from KUENEN's equations for the critical volumes and temperatures.

x	V_{xk}.	T_{kx}.	T_{Rx}.
1	0.00725		
3/4	606	402 (397.5)	396
1/2	620	350	370.1
1/4	489	338 (339.5)	331.4
0	435	304	

It is remarkable that (as follows from the values of n and the linear variation of b just mentioned and the relation $v_k = 3\,b + 2\,\beta$) the critical volumes show the same course as that found by means of the method of coincidence. From KUENEN's combined experiments it would hence appear that for mixtures of methylchloride and carbon dioxide the critical volumes cannot be expressed as a function of the second degree of the composition, as it is accepted by VAN DER WAALS in his theory of ideal mixtures, but that at least a function of the third degree is required for it.

In fig. 5 the curve of v_k is represented by a dot-dash-line when resulting from the coincidence method, and by a dash-line when resulting from KUENEN's equation, and by a complete line that of the ideal mixture to be considered in the next section.

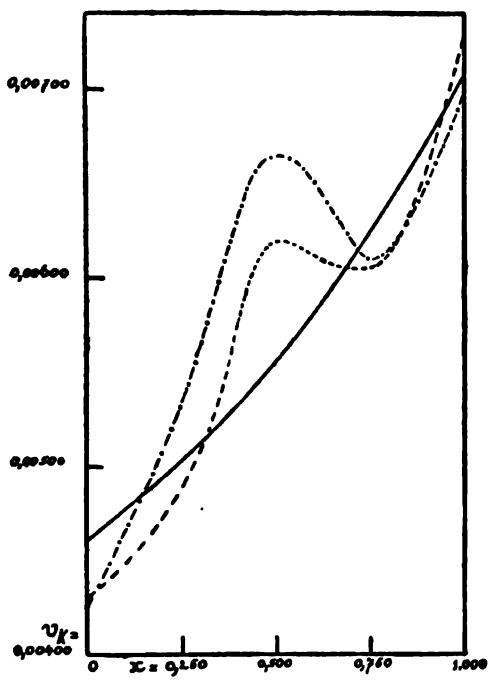

Fig. 5.

Concerning the critical temperatures, not much can be derived from KUENEN's equations. For the values between brackets in the table given above a has been calculated by means of $\frac{K}{T}$, in which we have used for K the numbers given in brackets by KUENEN. The temperature values without brackets in the same table have been

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calculated with values of a obtained by interpolation between the values of a given by KUENEN separately for different temperatures.

Only for the second mixture an acceptable value of $T_R - T_k$ is found, i. e. 20°, but it is obvious that this difference cannot be negative as with $x = {}^3/_4$ or zero as with $x = {}^1/_2$. And so the values from KUENEN's equations cannot be an argument either for or against the values found by means of the method of the coincident systems.

Therefore for the time being no arguments other than those derived from the deviations of the critical volume mentioned above, can be adduced to justify the doubt of the possibility of expressing the critical quantities of the homogeneous mixtures in the case of KUENEN's experiments by the formulae given by VAN DER WAALS for the critical quantities of homogeneous mixtures, together with KUENEN's, identity $Ta_x = K_x$.

§ 3. In order to obtain for $K_{11}, K_{12}, K_{22}, b_{11}, b_{12}, b_{22}$ in the equation

$$p = \frac{RT}{v - b_x} - \frac{K_x}{T(v + n\,b_x)^2}$$

$$K_x = K_{11}\,x^2 + 2\,K_{12}\,x\,(1-x) + K_{22}\,(1-x)^2$$

$$b_x = b_{11}\,x^2 + 2\,b_{12}\,x\,(1-x) + b_{22}\,(1-x)^2$$

(p = pressure in atmospheres, v = volume expressed in terms of the theoretical normal volume, R = gasconstant, T = absolute temperature, x = molecular composition, while the value of 1.4610 was taken for n) values which agree as well as possible with KUENEN's experiments, a curve of the second degree was drawn almost corresponding with the critical volumes found from the coincident systems, from which b_{11}, b_{12} and b_{22} were found. The convexity was chosen towards the x-axis, because in that case a value for K_{12} could be found, for which K_x was obviously of the second degree. This is justified as the final equations represented KUENEN's isothermals still within 2 pCt.

Subsequently the observation of the critical temperature of the point of contact for the mixture $x = {}^1/_2$ was taken as a basis for the calculation of the a's.

Now that the difference $T_{xR} - T_{xk}$ could not be deduced with any certainty from the observations, we had to confine ourselves to an estimation of it.

According to the results of the graphical determination of the connodal curve on a plaster cast constructed previously (see HART-

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MAN's figure derived from it, Communication N°. 59^a, § 3) the critical temperature of the homogeneous mixture is situated lower than the plaitpoint temperature and although the place remains very uncertain, we thought ourselves justified in searching it at double the distance.

For our purpose it seemed at any rate sufficient to subtract 7° from the temperature of the critical point of contact for the composition $^1/_2$. With $T_{R\frac{1}{2}} - 7° = T_{k\frac{1}{2}}$, T_{k0} and T_{k1} we could now calculate K_{11}, K_{12}, K_{22}.

When the plaster-cast of the part of the surface near the plaitpoint was ready, it appeared that for the ideal mixture supposed $T_{R\frac{1}{2}} - T_{K\frac{1}{2}}$ amounts to about 19° C. which deviates from the value first accepted in the sense of what had been derived from the observations of the mixture $^1/_2$ (i. e. 30° C. from the method of the coincident systems, 20° C. from KUENEN's equations.)

The following table gives the constants found and the critical quantities derived from their combination.

$K_{11} = 6.276$ $\quad b_{11} = 0.001193$

$K_{12} = 3.314$ $\quad b_{12} = 0.000893$

$K_{22} = 2.176$ $\quad b_{22} = 0.000780$

	T_{kx}	p_{kx}	v_{kx}
$x = 1$	416	64.8	0.007065
$x = {}^3/_4$	391	68.9	6249
$x = {}^1/_2$	363	71.8	5568
$x = {}^1/_4$	336	73.0	5022
$x = 0$	303	72.2	4620

The value of $\frac{p_k v_k}{RT_k}$ is thus found to be $= \frac{1}{3.33}$. The variation of p_k agrees with that of p_R (see the usual pT diagram).

§ 4. In the construction of the detailed plaster-cast it was important not only to profit by the opportunity of being able to choose a larger scale for v and x with almost unchanged dimensions of the whole model, but also to make the curvature of the w-surface

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near the plaitpoint as well defined as possible and thus to make the determination of the connodal curve and the tangent chords as accurate as possible. As now the surface near the plaitpoint is but little removed from its plane of contact, an enlargement of ψ, by which the differences $\psi'' = \psi - \psi_c$, where ψ_c is the value of ψ for points in the tangent plane lying at the same values of x and v, are enlarged in the same proportion, will cause the surface as a whole to become much more inclined with regard to the xv-plane, which again would cause the model to have only limited dimensions in the x- and v-directions with the same dimension in the ψ-direction, in order to make the curvature more prominent. We have avoided this difficulty by constructing a model in which the properly magnified values ψ'' of $\psi - \psi_c$ for x and of v as independent rectangular variables are measured perpendicularly to the xv-plane. In this way the general oblique position of the surface with regard to the vx-plane is eliminated, and $\psi - \psi c$ can be enlarged as much as is allowed by the greatest dimension which we wish to give to the model in the ψ co-ordinate, through which the curvatures become prominent as desired. The plane of contact on this model if continued to $v = \infty$ would become for $x = 1/2$ and for $v = \infty$ a-plane sloping to the xv-plane with the angular-tangents a and b, whereas in the case of the ψ-surface it would be parallel to the xv-plane.

ψ_c in $\psi'' = \psi - \psi c$ is a linear function of x and v. VAN DER WAALS has already demonstrated that the addition of a linear function in x does not influence the properties which are of importance in the thermo-dynamical consideration of the ψ-surface. This holds good also for a linear function of v.

Putting $\psi' = \psi + av + bx$ we get

$$\frac{d\psi'}{dx} = \frac{d\psi}{dx} + b$$

$$\frac{d\psi'}{dx} = \frac{d\psi}{dv} + a$$

$$\mu_1' = \psi' - v\frac{d\psi'}{dv} - x\frac{d\psi'}{dx} = \psi - v\frac{d\psi}{dv} - x\frac{d\psi}{dx} = \mu_1$$

$$\mu_2' = \psi' - v\frac{d\psi'}{dv} + (1-x)\frac{d\psi'}{dx} = \psi - v\frac{d\psi}{dv} + (1-x)\frac{d\psi}{dx} = \mu_2 - b\,.$$

For the shape of the projection of the curves $\frac{d\psi''}{dx} = \text{const.}$ $\frac{d\psi''}{dv} = \text{const.}$ $\mu_1 = \text{const.}$ $\mu_2 = \text{const.}$ on the xv-surface it is of no

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consequence whether each is increased by a constant quantity, for in the case of μ_1 there is not even difference between the two values of the quantities μ_1 and μ_1'.

The values of ψ'' used for the construction of the model and the drawings are determined in connection with the absolute values of ψ used in the general model of the whole plait (comp. Communication 59[a]) by means of the following equations.

$$\psi'' = -31786\ \psi - 0{,}25\ v + 48000\ x - 164780$$

$$-\psi = \int_{\infty}^{v} p\,dv - R\,T\,(x\,lg\,x + (1-x)\,lg\,1-x) + 9.4383.$$

§ 5. Plate III is a photographic representation of the detailed model on which the connodal line and the tangent chords are shown, the depth of the plait is made clear by the shadow of the tangent lines. Fig. 1 and 2 Pl. IV shows the sections $\psi''_x = f(v)$ and $\psi''_x = f(x)$. Pl. IV fig. 3 shows the pressure-curves $\frac{d\psi''}{dv}$ = const. and the substitution-curves $\frac{d\psi''}{dx}$ = const., fig. 4 represents the pressure curves and the potential curves $\mu_1' = \mu_1 = \text{const.}$ (all this on the $v\,x$-surface). In the two last figures x is ordinate and v, in $\frac{1}{100000^{\text{th}}}$ parts of the theoretical normal volume, is abscissa.

In fig. 3 and 4 the connodal line has been shown as a dot-dash line, a shadow approximately indicates how great is the uncertainty of this line. The exact place of P (the plaitpoint) on the connodal line is still fairly uncertain. A detailed investigation like the foregoing would again be required with regard to a limited part round P. A similar investigation of the two parts round the two points of contact of a tangent-chord will give us greater certainty as to the exact situation of that tangent chord. So the point R (the critical point of contact) can also still be better fixed.

It may be assumed that we have nearly obtained the difference $x_{TR} - x_{TK}$ of the composition ratios of critical point of contact and of the plaitpoint at the temperature $T = 373°$ C. From this by a better estimation more suitable values can be derived for the difference $T_{R^1/_2} - T_{K^1/_2}$, from which we started for the deduction of a_{12} etc., through which again values for a_{12} etc. could be found, from which a better agreement with KUENEN's experiments near the plaitpoint is to be expected.

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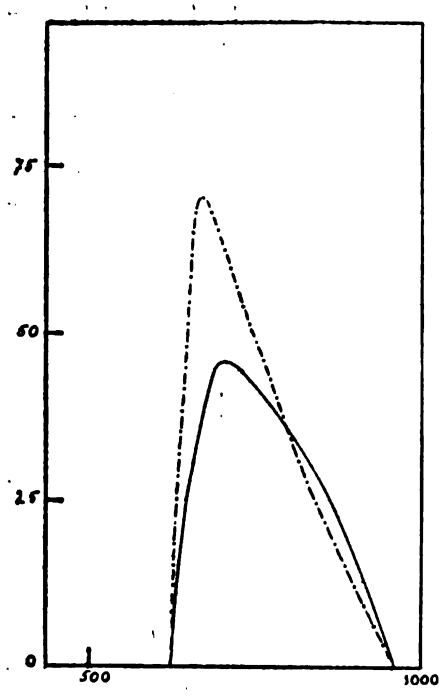

Fig. 6.

When we trace by means of the graphically found connodal line, the condensation phenomena for a mixture with composition x between the plaitpoint composition x_{PT} and the critical point of contact composition x_{RT} this will give us a representation of KUENEN's observations at 103° C. and the composition 0.41, which representation however will only be an approximation. Fig. 6 is obtained by reading on Fig. 4 Pl. IV for each a the relation of $\frac{S_{2a}}{S_{1a}+S_{2a}}$, the ratio to the whole tangent-chord of the piece from the intersection with the line which has the composition x (for which we want to investigate the condensation phenomena) to the contact on the vapour side — which ratio gives the number of molecules in the liquid state — and by determining from this the liquid volume at the tangent-chord a by multiplication with v_x. In the figure[1]) the liquid volume has been measured as ordinate of the curve and the total volume as abscissa.

The dotted line is KUENEN's curve. The composition for which the construction has been made has been chosen so, that the beginning and the end of the condensation are in the same ratio as in KUENEN's observations.

By reading the values of the pressure at the points of intersection of the tangent chords in fig. 4. Pl. IV, we find that the pressure during the condensation varies almost linearly with the total volume. This is also very nearly the case in KUENEN's experiments. Also the amount of the pressure is in fairly good agreement. While KUENEN found an increase of 73,5—83,8, we find from our figure one of 78,6—93,2.

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[1]) Compare also the figure for the retrograde condensation in mixtures of carbon dioxide and hydrogen. VERSCHAFFELT, Comm. 45, fig. 2 on the plate (Proc. Acad. Amst. Dec. '98.

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Dr. H. KAMERLINGH ONNES and Dr. M. REINGANUM. „Contributions to the knowledge of VAN DER WAALS' ψ-surface." II. „The part of the transverse plait in the neighbourhood of the plaitpoint in KUENEN's experiments on retrograde condensation."

PLATE III.

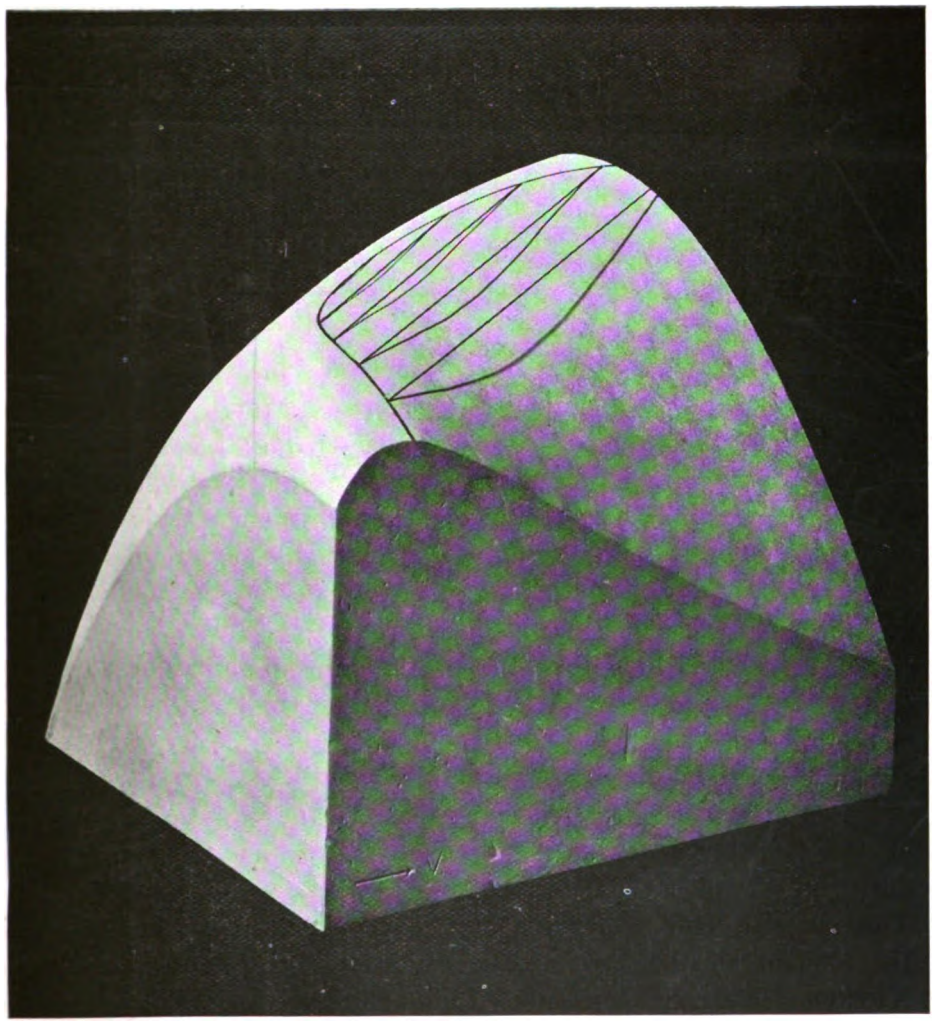

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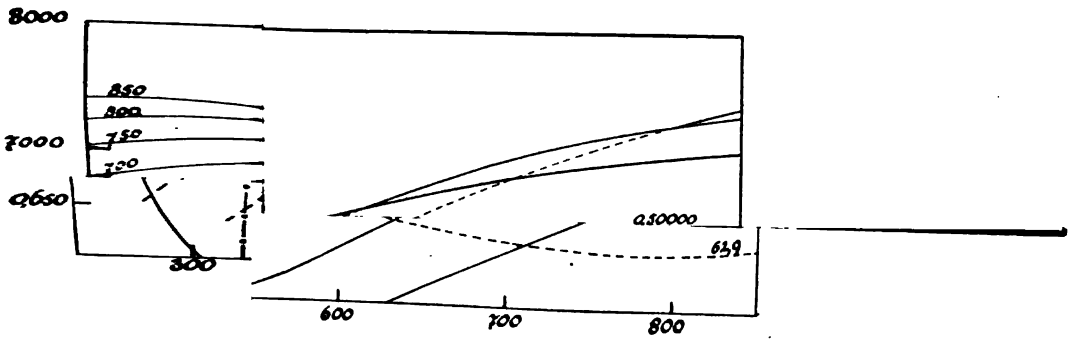
PLATE IV.

1.



Proceedings Royal

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Physics. — Communication N°. 60 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES and M. BOUDIN. "*On the measurement of very low temperatures.* III. *Coefficient of pressure variation of pure hydrogen between* 0° *and* 100°".

(Read June 30, 1900.)

15. Very careful determinations of the coefficient of pressure variation of pure hydrogen, described by one of us (H. K. O.) in Communication N°. 27 § 8 (Communication to the meeting of June 1896 of which this paper is a continuation) have now been made with the large pattern (comp. N°. 27 §§ 2 and 3) of the constant volume hydrogen thermometer for low temperatures.

This determination comprises, [the bulb of the thermometer being placed in ice (l.c. § 7) or in steam (l.c. § 8)], measurements of the temperature in the different parts of the apparatus, and lastly measurements of the volume occupied by the gas.

16. *The measurement of the pressures.* The pressure are determined by the difference in height of the mercury menisci in the manometer (§ 2) augmented by the pressure which is exerted on the outer level of the manometer and which is indicated by a mercury barometer placed beside the apparatus [1] [2]). The level of the top and the height of the meniscus are read for each of the menisci by a cathetometer. From the height we derive the correction for the capillarity according to MENDELEJEFF's table. The temperature of each of the mercury-columns is read on thermometers, placed symmetrically. Moreover we allow for the difference in height between the top of the manometer column and the lower meniscus of the barometer.

The manometer-tube has been described in §§ 2 and 3. The barometer the tube of which has a diameter of 14 m.m., has been previously boiled very carefully in vacuo and is protected by a drying tube.

The transportable cathetometer, constructed by the Société Genévoise is an exceedingly good instrument, arranged for differences in height up to 110 cm., and provided with 3 telescopes [3]) in order

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[1]) By dividing the mercury column which indicates the pressure of the gas in two parts, we avoid the great difficulty which arises whenever we read great differences of level owing to the unmanageableness of the cathetometer required for this.

[2]) For measurements in which quick reading is more important than high precision, we use an aneroide as WIEBE and BÖTTCHER did. Ztschr. f. Instr. X. p. 26. 1890.

[3]) CHAPPUIS on his stationary cathetometer has used 3 telescopes in order to read 3 menisci. Mém. Bureau Intern. T. VI. p. 31.

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to read the 4 menisci. For both accurate and quick reading it is of great advantage, not to be obliged to move the slides over the vertical column. Therefore the two lower (or upper) menisci are placed at about the same height and read with the lower (or upper) telescope; the two upper (or lower) menisci with the two other telescopes [1]). A difficulty arises whenever the difference of level to be measured would lie between about 1 and 10 c.m. Then we cannot adjust for the two levels either with one or with two telescopes, as the construction of the slides does not allow the telescopes to be brought to a smaller distance from each other than 10 c.m. The difficulty might be solved by using a fourth telescope or another cathetometer with two telescopes. But in § 18 a method is described by which the difficulty can be avoided, so that we have always been able to read the 4 menisci with one cathetometer and only 3 telescopes without readjusting these. Each of the telescopes is provided with an micrometer-eyepiece (screw-thread 0.25 m. m., and head divided into 100 parts). The micrometer screws have been tested on the exceedingly good apparatus for the measurement of photographic star-plates at the Leiden Observatory, constructed by REPSOLD according to H. G. VAN DE SANDE BAKHUYZEN'S [2]) indications, which apparatus had kindly been placed at our disposal. The progressive error remained except in one or two teeth (revolutions) below 2 micron. For one of these micrometer screws the formula for the periodic error was computed [3]). This was found to be $\varphi(u) = 0.402^5 \cos. u - 0.730 \sin. u$ in divisions of the head, so that for repeated adjustments we may regard this as negligible. The collimation difference of the telescopes have been measured in pairs at long intervals by different observers, the telescope-slides having been removed in the mean time from the cathetometer-tube and again replaced on it, while the telescopes had been completely taken to pieces. Still it was found after reading on the verniers of the slides:

I—II	Dr. DIJKEN	direct	50.26	mm.
I—II	BOUDIN	„	50.27	
III—II	„ 3.12	indirect	50.26	
III—I	„ 53.38			
III—II	„ 3.13			

[1]) In the very diagrammatic figure 1, Pl. I, Comm. 27, only two telescopes have been drawn.

[2]) H. G. v. D. SANDE BAKHUYZEN, Mesure des clichés d'après la méthode des coordonées rectangulaires (Bulletin, Comité de la Carte du ciel, 3e fasc. 1889.)

[3]) F. KAISER, Eenige opmerkingen omtrent de periodieke fouten van Micrometerschroeven. (Versl. en Med. K. Akad. v. W. Amsterdam, 2e Reeks, Deel 1. 1866.)

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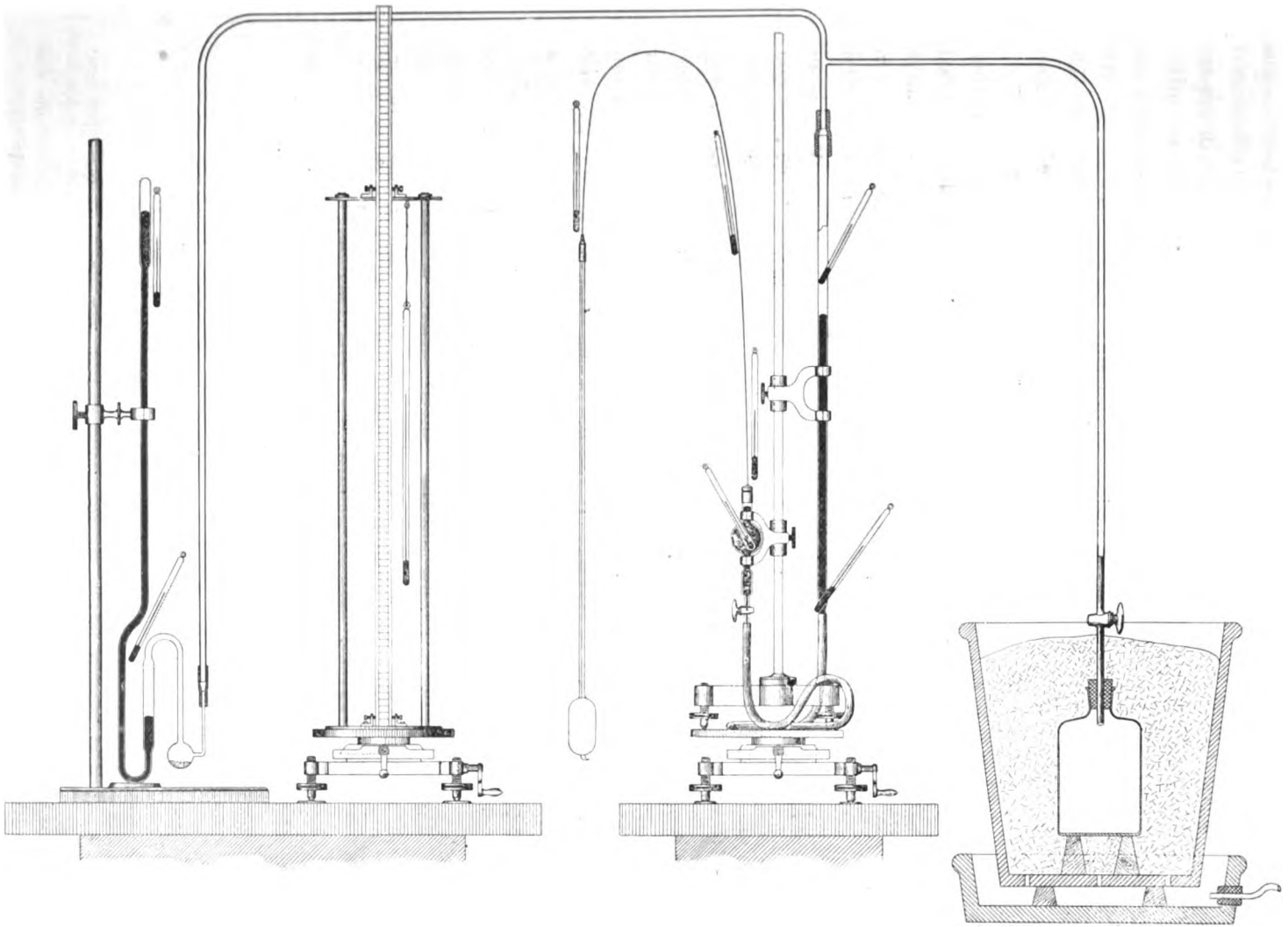
Dr. H. KAMERLINGH ONNES and M. BOUDIN. "On the measurement of very low temperatures.
III. Coefficient of pressure variation of pure hydrogen between 0° en 100°". PLATE VI.



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The correctness of levelling of the cathetometer was tested by the menisci in two communicating mercury-tubes, presenting a difference of azimuth of 90°, and no difference in height amounting to 0.01 m.m. was found.

The levels have been tested by the level-tester and tables have been made of the corrections at distances of 10, 20, 30, 50 c.m. Each time a micrometer head was read, the level on the telescope was also read. The method we followed was to read the difference in level observed through the telescopes on a divided bar scale [1]), not on the cathetometer-scale itself. For this purpose we used a standard meter constructed by the Société Genévoise [2]) of 120 c.m. length, mounted on a special stand made in the work-shop of the laboratory which could turn round a vertical axis and was provided with adjusting screws, rendering it possible to adjust the bar by means of the cathetometer itself to a vertical position. (See Pl. VI this paper).

17. *The adjustments.* The barometer, the manometer, the divided bar, and the cathetometer are all mounted on stone pillars fixed to a freestone slab, which in its turn rests on one of the fixed pillars of the laboratory. The stones are easily mounted and temporarily consolidated by means of plaster to a rigid block of stone.

In order to be able to adjust accurately, the focussing of the telescopes not being altered, it is necessary that two of the three apparatus should be movable. To attain this they are placed on carefully worked metal stands (see Pl. VI of this paper) which can be moved in two directions at right angles by micrometer screws with handles. Tho manometer and the scale are placed on the stands; the barometer and the cathetometer are firmly mounted and the telescopes focussed on the barometer menisci. Then the divided bar is placed vertically and brought at the required distance by means of the screws. The adjustment of the manometer into position is more difficult; the best way is to bring one of the sliding motions of the double sledge on which the apparatus is placed in the direction of the cathetometer, and then to turn the stand and bring

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[1]) CHAPPUIS l.c. p. 31. We ascertained by a great number of measurements, that it was not necessary to read the scale immediately after a meniscus, but that the menisci could be read successively and the scale at the beginning or at the end of the series of measurements.

[2]) ISAACHSEN's test of H_{12} has shown the great accuracy of these divided bar scales, comp. Bureau Internat. l. c. p. 39.

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the menisci at the same distance from the cathetometer and to adjust them with the screw both at the same time.

18. *The elimination of variations in the barometer pressure.* Rapid variations of the atmospheric pressure are an important cause of uncertainty in these measurements of pressure [1]). Though the telescopes need not be moved along the scale, yet some five minutes must elapse before the reading of the four heights is complete, and during this time the variations in barometric height are often not negligible.

For example the readings on the 15th Febr. were

2^h	762.50
2^h30	761.92
3^h	761.51
3^h30	761.30
4^h30	760.80

Obviously the resulting uncertainty can be much diminished by a suitable combination of the observations in special cases of the variation. Suppose for instance that the changes in atmospheric pressure p are linear with time t so that we may put $p = p_0 + \pi t$, further suppose that the changes in both limbs are equal and opposite in sense, equally well in the barometer and manometer. When $t = 0$, let n_1 be the lower level, n_2 the upper level for the manometer, n_3 and n_4 the same for the barometer, further suppose that the levels are reread at intervals of one minute and that in the formula mentioned the time is measured in minutes. The real pressure is then $n_2 - n_1 + n_4 - n_3$. If we read in the order n_1, n_4, n_3, n_2 then the actual readings are n_1, $n_4 + \pi$, $n_3 - 2\pi$, $n_2 - 3\pi$.

From this we derive

$$[n_2 - 3\pi - n_1] + [n_4 + \pi - n_3 + 2\pi] = (n_2 - n_1) + (n_4 - n_3).$$

The combination n_3, n_1, n_2, n_4 leads to the same result, while the insertion of the barometer reading between two manometer readings as n_1, n_2, n_3, n_4, n_1, n_2 also eliminates a linear rise or fall of the atmospheric pressure.

We can also find a number of combinations by which a parabolic variation can be eliminated.

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[1]) Regnault, Mém. de l'Inst. XXI p. 69 says: Je ne crains pas d'exagérer en posant en fait, qu'on ne peut pas répondre d'une mesure barométrique à plus de $^1/_{10}$ de millimètre, quelque perfectionnés que soient d'ailleurs les appareils de mesure.

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Thus let $p = p_0 + \pi t + \varkappa t^2$.

A first reading $n_1 n_4 n_3 n_2$ gives	a second $n_3 n_2 n_1 n_4$ gives
n_1	$n_3 - 4\pi - 16\varkappa$
$n_4 + \pi + \varkappa$	$n_2 - 5\pi - 25\varkappa$
$n_3 - 2\pi - 4\varkappa$	$n_1 + 6\pi + 36\varkappa$
$n_2 - 3\pi - 9\varkappa$	$n_4 + 7\pi + 49\varkappa$
$n_4 - n_3 + n_2 - n_1 - 4\varkappa$	$n_4 - n_3 + n_2 - n_1 + 4\varkappa$

so that the mean of both gives the pressure at time zero independant of π and $\varkappa$.

But in the first place we have not eliminated by this process the capricious variations of pressure which often are of considerable importance, and moreover if the pressure in the manometer had been correctly determined at a given moment, we are not even then entitled to assume that this is the pressure of the gas in the reservoir. Especially to be certain of the latter it is desirable to remove as far as possible the variations in the pressure.

To this end the manometer-tube is connected with the open limb of the barometer by glass tubes of 3 m.m. diameter well packed in wool (the wool packing has not been drawn on the plate, in order not to render the drawing indistinct). In order to diminish the variations of the pressure which accompany the variations in temperature of the air contained in these tubes, a bottle of 2 liters capacity is included in the connections, this bottle being always immersed in ice shavings prepared with the precautions of § 7 [1]).

The total volume of gas contained in the manometer, barometer and connecting tubes which is exposed to variations of temperature is about 60 c.c. and thence the variation of pressure resulting from a change of temperature of 1 deg. C. will be only 0.07 to 0.08 m. m. This change can only take place so very slowly and regularly that it may be eliminated by the choice of the order of observations according to the above mentioned method. In a complete series of observations the variations are always less than 0.1 m. m. and are very regular. Thus on the 10th March we observed

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1) The whole apparatus can now be considered as a differental air thermometer. We think that PFAUNDLER first used such an apparatus Sitzb. Wien (2) LXXII, 729. 1876. We found further that CALLENDAR has proposed to connect the constant pressure air thermometer with a space at standard pressure in order to avoid the reading of mercury columns. Phil. Mag. 5. 48. p. 540. 1899.

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3^h	750.47
3^h30	750.50
4^h	750.51
4^h30	750.52

This arrangement also allows us to avoid the difficulty mentioned in § 16 as arising from reading the four menisci with only three telescopes. We have only to alter the pressure by a few centimeters in the reserve bottle and in the tube connecting the barometer and manometer with it in order to arrange that two of the menisci are read either by one or by two telescopes.

19. *Determination of the temperatures.*

We must know the temperature of the reservoir and of the different parts of the connecting space, which latter consists of the thermometer capillary outside the constant temperature bath, the steel capillary and the volume near the point of the manometer-tube (comp. Comm. N°. 27 § 2 and Pl. II, fig. 4[a]) where the adjustments of the meniscus for constant volume are made.

During the determination of the zero the thermometer reservoir and about 30 cm. of the capillary are immersed in shavings of ice (§ 7). A thermometer gives the temperature of the remainder of the capillary which has only a very small volume.

Three thermometers are placed against the steel capillary and divide this into two parts for the temperature of each of which we assume the mean of those observed at the ends.

For the temperature of the volume near the steel point we read the last thermometer on the steel capillary and those on each side of the manometer. These differ only by two or three tenths of a degree.

During the determination of the boiling-point the reservoir and nearly the whole of the glass capillary is immersed in the boiling apparatus. The temperature of ebullition is computed from BROCH's tables [1]), in connection with which we used the value $g = 9.81318$ [2]) at Leiden. The difference of pressure observed by the small water manometer (comp. § 8), was allowed for.

The atmospheric pressure is read by an aneroide, which is repeatedly controlled by the barometer.

The remaining 10 cm. of the capillary reach above the boiling

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[1]) GUILLAUME, Thermométrie de précision, pag. 327.

[2]) Determination by DEFFORGES and BOURGEOIS 1892.

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apparatus; for this part the mean of the temperature of the boiling apparatus and of the first thermometer against the steel capillary was taken; the temperature of the steel capillary itself is accounted for as in the determination of the zero.

Special precautions have to be taken, that the temperature of the steel capillary should not be too uncertain owing to the rising hot vapours and radiation.

At a time when the steel capillary was packed only in wool, but otherwise the arrangement of the boiling apparatus was that shown in Communication N°. 27 Pl. III, fig. 1 we read on the three thermometers:

3^h 30	20°.7	14°.3	13°.5
4 30	20°.6	14°.3	13°.4.

And so the means were rather uncertain, due especially to the conduction of heat which takes place at the beginning of the capillary.

To secure a more satisfactory protection of the capillary an india-rubber spiral with water-circulation was placed on the thick wool packing of the boiling apparatus, above this again large sheets of paper were stretched at a few centimeters distance from each other. Where the capillary passed through these protecting layers, which shielded it from radiation care was taken that it fitted well in the openings so that no hot air could pass.

The ascending hot vapours at the sides of the boiling-apparatus were conducted at two meters distance from this through a chimney made also of large sheets of paper, which were slightly inclined and fitted well against the apparatus. With these simple arrangements we succeeded in keeping the differences of temperature along the capillary within the same limits as in the zero-determinations, and hence they only depend upon the temperature of the room.

Thus on March 10 we observed:

3^h	15°,6	15°,2	15°
4^h30	15°,4	15°,1	14°,5

No special precautions were taken to keep the temperature of the room constant. It is not difficult by means of heating and ventilating to arrange that the variations of temperature do not exceed 1 deg. C. in a series of observations.

The influence of the various sources of error resulting from the uncertainty of the temperature determinations is considered in § 24.

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20. *The measurement of the volumes.* The calibration of the glass parts of the apparatus has been described in § 2. The steel capillary has first been separately calibrated (filled by means of the mercury pump), and again after having been connected to the volumenometer tube, in which case they are also filled by means of the mercury pump. In this way the whole connecting space is determined at one time. As the upper part of the volumenometer tube has also been calibrated (Comm. N°. 27, p. 6) the two methods include a mutual test.

3 measurements by the first method gave on an average 749 mm³.[1])
5 „ „ „ second „ „ „ „ „ 752 „

The volume of the meniscus which we want for the determination of the volume of the gas shut off by it, cannot in a tube of the dimensions used, be considered as a constant[2]), derived from the diameter and a definite assumed angle of contact. For the height of the meniscus varied between 1.38 m. m. and 1.54 m. m., which corresponds to a change of volume of about 10 m.m.³, if the top of the meniscus is stationary, an accidental error that cannot be admitted as we shall see later. The volumes are computed in each case from the height and the diameter like that of a spherical segment. The systematic error which then remains may be considered to be small enough to be neglected (comp. § 24). We intend to determine this volume still more accurately by fixing several points, say three, to the upper surface of the connecting space, along one diameter, and to measure the vertical distance of each of these 3 from the mercury, in order to determine the true profile of the meniscus.

As a meniscus of 1.46 m.m. height occurred repeatedly, we have considered this as the normal meniscus in a way to be later described more in detail.

The coefficient of dilatation of the Jena-glass 16^{III} used indicated by k was determined by us between 0° C. and 100° C. according to the method of the weight-thermometer. We found $k = 0.0000242$. The small difference from the value generally given for 16^{III} i. e. 0.0000244 [3]) does not exceed the probable error. The variation of

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[1]) The value 750 mm³. was taken after comparing the accuracy of each method.

[2]) As done by CHAPPUIS l. c. p. 51.

[3]) WIEBE and BÖTTCHER l. c. give 0.0000240.

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the volume under the influence of the pressure was determined as in § 2. With a pressure of 1 atm., the variation of volume of the reservoir was 4.64 m.m.^{3} at 15° C. We intend to determine the amount of this correction for 0° C. and for 100° C. separately. For the time being we have applied the correction found for 15° invariably at 0° C. and at 100° C.

Fig. 5.

21. *Modifications in the thermometer.* Since the description given in l. c, § § 2, 3, 4, the following small alterations have been made. In l. c. Pl. II fig. 4 we see that the cap with its capillary is pressed onto the ground glass capillary of the thermometer-stem. But we cannot then be quite sure that a perfect contact between the cap and the upper side of the stem is obtained, and if this is not the case the connecting space would be augmented by an unknown amount. Now however to the end of the thermometer capillary another, somewhat wider one (2 m. m. diameter) is sealed on, into which the steel capillary is placed (see fig. 5). This passes through the whole length of the cap and projects beyond it for a few millimeters at the other end. The connection then is made as in the case of the volumenometer (l. c. § 4) the space between the capillary is entirely filled with sealing wax, the glass capillary is then placed into it, which is easily done without there being any danger of the steel capillary becoming blocked, as it projects a few m.m. above the cap.

To mark off the irregular part of the capillary near the joint, two marks are made on the glass. The volume of the space between these marks has been accurately determined, as well as the sections of the glass and the steel capillary; so that the exact volume is known.

The connection of the volumenometer with the larger steel cap on the steel capillary has on the whole remained the same. Instead of sealing-wax we now use marine glue so as to render the chance of cracks (causing uncertainty in the connecting space) and leakage less. But this method requires the cap to be fixed by copper wire in order to prevent it from being pushed off by the soft marine glue under the pressure which obtains in the thermometer during the determination of the boiling point. Lastly the small tube in fig. 1 and fig. 7. Pl. II l. c. is not sealed off any longer, but it is now provided with a small glass cock. As the apparatus has already been provided with a cock (*k* ibid.), this does not involve any new

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difficulty; the new cock is very useful whenever we want to alter the pressure of the gas, or to fill the thermometer with another gas.

22. *The preparation of the pure hydrogen.* The apparatus used for this purpose (l. c. § 5) has also undergone a few small alterations. In the first place several indiarubber connections have been removed. The two storage-bottles for hydrochloric acid and potassium hydroxide solution (*d* and *e* fig. 3 Pl. I comm. n°. 27) are now like the WOULF'S wash bottle closed with ground stoppers and the screw clamp *C* has been replaced by a mercury-closure. The large drying-towers *i*, *i* are replaced by a *U*-shaped tube, closed with ground glass stoppers. Even with careful heating of both the glass and the india-rubber, it requires much care to make india-rubber fittings on glass by means of sealing wax perfectly trustworthy; if as often is the case some solution of india-rubber is applied between the glass and the india-rubber, the solvent evaporates in the vacuum and the high degree of purity, as we require it for our hydrogen, is altogether lost.

Lastly for the preliminary filling we no longer use commercial hydrogen, but hydrogen prepared from pure zinc and hydrochloric acid in a separate glass apparatus.

23. *The calculation of results.* Our determination comprises the reading of the menisci and of the various thermometers.

Suppose the reservoir is at $t°C$. Let H_T be the pressure of the included gas corrected for the temperature of the mercury and the compression of the latter under its own weight (to be neglected); the correction applying for the value of gravitation will be discussed later.

Let V_o be the volume of the reservoir at $0°\,C$ and under the pressure of the gas during that time.

u_1 the volume of that part of the glass capillary which is at the temperature t of the reservoir.

u_2 the volume of that part of the glass capillary which is not at the temperature of the reservoir but at the temperature t_2.

u_3 and u_4 the volumes of those parts of the steel capillary where the temperatures are t_3 and t_4.

u_5 the volume near the steel point in the volumenometer.

β the variation of the volume V_o of the reservoir caused by the pressure.

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The volume u_5 and the temperatures are different for different determinations, therefore it is desirable to apply corrections which reduce them to a definite volume u_5 and definite temperatures.

From the temperatures observed we calculate the pressure, which would be found under the following circumstances: the whole of the thermometer capillary is reduced together with the glass reservoir to the same temperature $\theta°C$, differing very little from t. Moreover the entire connecting space must be reduced to 15° C and this space must be closed by a meniscus of 1.44 m.m. height touching the point of adjustment in the volumenometer-tube. Let u be the connecting space thus determined. Under these circumstances the following equation will hold for the pressure, which we call the reduced pressure H_θ.

$$H_T \left[\frac{V_0(1+kt)+\beta+u_1}{1+\alpha t}+\frac{u_2}{1+\alpha t_2}+\frac{u_3}{1+\alpha t_3}+\frac{u_4}{1+\alpha t_4}+\frac{u_5}{1+\alpha t_5}\right]=$$

$$(1) \qquad = H_\theta \left[\frac{V_0(1+k\theta)+\beta+u_1+u_2}{1+\alpha\theta}+\frac{u}{1+\alpha 15}\right],$$

in which k is the coefficient of expansion of the glass and α the coefficient of pressure variation of the gas between 0° C. and $\theta°$ C.

The differences of the small u's at the temperature of calibration and at the temperature of observation are too small to be accounted for [1]). The corrections from H_T to H_θ are made with an approximate value of α, for which we took 0,003662.

The values of θ, which are now important to us, are 0° C. and 100° C. For all corrections at the same temperature the value of H_θ is a definite amount, which therefore can be calculated once for all. The calculation of the value between [] to the left may be shortened by computing tables of the values of $\frac{u_n}{1+\alpha t_n}$, as the temperatures t_3, t_4, t_5 never deviate much from 15° C. [2]).

The pressures reduced in this way correspond therefore to the following circumstances:

At 0° C. a volume $V_0 + u_1 + u_2$ at the temperature 0°

" " u " " " 15°

At 100° C. the volume of the reservoir has become

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[1]) As for u_1, this volume itself is extremely small, and as for u_2, u_3, u_4, u_5 the difference of t_2, t_3, t_4, t_5 from the assumed standard temperature 15° C. is very small.

[2]) CHAPPUIS l. c. pg. 55.

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$$V_0(1 + 100\,k) + \beta,$$

and hence the circumstances are:

$V_0(1 + 100\,k) + \beta + u_1 + u_2$ at the temperature 100°

u " " " 15°

α is then found from [1])

$$H_0\left[V_0+u_1+u_2+\frac{u}{1+15\alpha}\right]=H_{100}\left[\frac{(V_0+u_1+u_2)(1+100k)+\beta}{1+100\,\alpha}+\frac{u}{1+15\alpha}\right]$$

$$(1+100\,\alpha)\left\{1-\frac{u}{V_0+u_1+u_2}\;\frac{1}{1+15\alpha}\;\frac{H_{100}-H_0}{H_0}\right\}=$$

$$=\frac{H_{100}}{H_0}\left[1+100k+\frac{\beta}{V_0+u_1+u_2}\right] \quad (2)$$

This equation can be solved by successive approximations, bearing in mind that H_{100} and H_0 include corrections depending on α. H_{100} and H_0 might then be computed anew with the new value of α, and the equation solved anew. The number 0,003662 used by us in the first approximation is in such good agreement with the correct solution, that in this case it was not necessary to make a second series of calculations.

24. *Influence of errors* [2]). $100\,d\alpha = \frac{dh}{H_0}$ is easily found when dh is the error in one of the determinations of pressure H_{100} or H_0.

For the accuracy of reading with a cathetometer we may assume $dh = 0{,}^{mm}01$ mm., and to this value corresponds $d\alpha = 10^{-7}$, an error which will be perceptible as a unit in the seventh place of decimals and would change the value 0,0036627 into for example 0,0036628. The other errors are best considered by reducing them to errors in the reading of pressure. As for the connecting space which as compared to the reservoir was very large (over 0,01) [3]) owing to the special arrangement of the thermometer for very low temperatures, a reading error in the distance from the meniscus to the point of 0,01 mm., which corresponds to 1,2 mm^3 error in u, gives an error

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[1]) Comp. CHAPPUIS l.c. p. 52.

[2]) Comp. CHAPPUIS, l. c. p. 56.
WIEBE en BÖTTCHER, Zeitschr. f. Instrumentenkunde 10, p. 233. 1890.

[3]) As in the case WIEBE and BÖTTCHER l.c.

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of 0,01 mm. in the pressure at the zero or 0,02 mm. in the pressure at the boiling point; incorrect determination of volume of parts of the connecting space causes a similar systematic error.

The capillarity leaves an uncertainty which we estimate at less than 0.03 m. m., the volume corresponding to the uncertainty of the form of the meniscus remains below 3 m. m.^{3}, corresponding to 0.03 m. m. and 0.06 m. m. in the pressure; the systematic error, which thus can arise in α does not reach 3.10^{-7}.

An error of 0.°01 C in the boiling point gives an error of 0.04 in the pressure; 0.°2 C error in the temperature of the capillary changes the pressure about 0.01 m. m. near the zero. In this respect no other than accidental errors are to be feared. Taking all together an accidental error of say 3 units in the last decimal (10^{-7}) is to be feared. The systematic error may reach the same value.

To illustrate the favourable influence of the precautions mentioned in §§ 18 and 19, especially of those relating to the removal of the variation of the atmospheric pressure, we give here a few observations of the zero, made in February without these precautions but otherwise under the same circumstances as the series of March in § 26.

In February we found on 4 days:	In March we found on 3 days:
$H_0 =$ 1098.24	$H_0 =$ 1098.35
1098.15	1098.36
1098.08	1098.37
1098.65	

In the first series the deviation from the mean rises to 0.4 m.m., which corresponds to nearly 0°.1 in temperature, a sufficient accuracy it is true for most determinations at low temperatures, but much smaller than we have attained with our apparatus when all the above mentioned precautions have been taken. The deviation 0.01 m. m. from the mean in the series treated in the latter way corresponds to 0°.02 or as mentioned above to a unit in the seventh decimal of the coefficient of pressure variation.

At the boiling point we found on 3 days (comp. § 26).

$$H_{100} = 1491.04$$
$$1491.00$$
$$1491.05$$

The deviation is here twice as large, but yet exceedingly small, whereas formerly, when the capillary was not so well protected, deviations of several tenths of m. m. occurred.

It is therefore useless to consider the previous determinations of the zero and the boiling point with a view to the coefficient of

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pressure variation to be derived from each pair of them. These are only of importance for the measurements at very low temperatures made at the time.

25. *Survey of a determination.* In the annexed table all the readings of one determination are given, but in order not to make the *scheme* too intricate the means of usually three single readings which never differ by more than a few hundredths, are given as the normal readings.

Column A gives the reading on the micrometer heads of the cathe-

	March 10	3 10	A.	B.	C.	D.	E.	F.	G.	H.
	Point.		24.19	5.5	1028 1029	23.42 25.51	5.5 5.5			
Manometer.	lower meniscus.	top.	24.36	5.5	1028 1029	23.42 25.51	5.5 5.5			
		basis.	27.44	6.0	1029 1030	25.51 27.61	5.7 5.7	15°0 14°8	16°2 15°8	14°5
	upper meniscus.	top.	20.37	7.0	282 283	18.86 20.86	7.0 7.0	15°6	15°6	
		basis.	21.97	7.0	283 284	20.86 22.89	7.0 7.0			
Barometer.	lower meniscus.	top.	21.42	5.5	1027 1028	21.30 23.42	5.5 5.5			
		basis.	22.20	5.5	1027 1028	21.30 23.42	5.5 5.5	14°2 14°6		
	upper meniscus.	top.	7.88	6.0	276 277	6.70 8.73	6.0 6.0			
		basis.	8.99	6.0	277 278	8.73 10.75	6.0 6.0			
Manometer.	lower meniscus.	top.	24.41	5.2	1028 1029	23.42 25.51	5.5 5.5			
		basis.	27.43	6.0	1029 1030	25.51 27.61	5.7 5.7	15°2 14°0	16°5 16°0	14°4
	upper meniscus	top.	20.40	6.8	282 283	18.86 20.86	7.0 7.0	16°0	15°2	
		basis.	21.90	7.0	283 284	20.86 22.89	7.0 7.0			
	Point.		24.22	5.5	1028 1029	23.42 25.51	5.5 5.5			

Aneroïde 771.3 Temp. 14°,3
Water-manometer + 1 mM.

tometer telescopes, B gives the reading on the levels of those telescopes [1]), C the nearest division of the graduation on the standard-meter [2]), D and E the readings of the head and the readings of the

[1]) This reading is not mentioned by CHAPPUIS.
[2]) Comp. footnote 1, p. 6.

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levels during the adjustments to those divisions. The three last columns refer to the temperatures. F gives the temperatures readings of the manometer and the barometer, G those of the capillary, H of the standard scale.

With these numbers we first compute the readings on the standard-meter, with allowance for the levels. Then the thermometer readings are corrected.

In the next table column *A'* gives the level of the top of each meniscus and the value of the height of each meniscus.

Column B' gives this level corrected for the capillary depression. C' the corrected temperature of the mercury columns. D' the corrected temperature of the capillary. E' the sum of the mercury columns corrected for the temperature and lastly F' the distance from the top of the meniscus to the point.

		A'	B'	C'	D'	E'	F'
Manometer.	lower meniscus.	1025.45	1028 29	14°4			
	height.	1.46		13.9			
	upper meniscus.	282.76	282.69	15.0	15°6		
	height.	0.76			15°2	mm 1492.57	mm 0.09
Barometer.	lower meniscus.	1027.05	1027.05		15°0		
	height.	0.37		14.2			
	upper meniscus.	276.58	276.58	14.5			
	height.	0.54					

Pressure of the water-vapour 771. 6 m.m. Leiden.

" " " 771.25 level of the sea 45° L.

From the means in pairs of column D' follows the temperature of the capillary, from the height of the meniscus and the distance from the meniscus to the point given in F' follows the correction for the space between the horizontal plane through the point and the meniscus. A correction 0.07 m.m. for the difference in level of barometer and manometer is then applied to the pressure according to the law of the communicating tubes [1]).

[1]) The difference of pressure between reservoir and manometer — a correction the necessity of which was remarked by Dr. v. EVERDINGEN — could be neglected, the gas being hydrogen and the difference of level of reservoir and manometer small.

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So we get the following table:

Volume.	Temperature.		Pressure H_t
$V_0 (1 + k t) + u_1$	82.333	$t = 100°44$	
u_2	0.009	$t_2 = 60°$	mm
u_3	0.444	$t_3 = 15°4$	1492.50
u_4	0.306	$t_4 = 15°1$	
u_5	0.218	$t_5 = 14°7$	

The pressure has not been reduced here to the absolute value as in the case of that for the boiling water, because for the following calculations relative values are sufficient.

The reduced temperature H_{100} according to the equation I is now found from:

$$1492.50 \left[\frac{82.333}{1+100.44\alpha} + \frac{0,009}{1+60\,\alpha} + \frac{0.444}{1+15.4\,\alpha} + \frac{0.306}{1+15.1\,\alpha} + \frac{0.218}{1+14.7\alpha}\right] = 61,177\ H_{100}°$$

$H_{100} = 1491.03$ m.m.

(β can be left out in this reduction calculation.)

26. *Results.* Here follow the values found for H_0 and H_{100} from determinations according to the method § 25.

3 March	7 March	13 March
$H_0 = 1098.38$	$H_0 = 1098,38$	$H_0 = 1098.34$
35	37	30
29	32	38
31	33	mean 1098.34
29	32	
mean 1098,32	28	
	29	
	mean 1098.33	

2 March	8 March	10 March
$H_{100} = 1491.05$	$H_{100} = 1491.01$	$H_{100} = 1491.03$
05	01	08
07	1490.98	10
06	1491.00	00
1490.96	1490.98	mean 1491.05
96	1491.02	
mean 1491.02	mean 1491.00	

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The equation (2) of § 23 becomes with $100\,k + \frac{\beta}{V_o + u_1 + u_2} = 0{,}00245$

$$(1 + 100\alpha)\,(1 - 0{,}00395) = \frac{H_{100}}{H_o}\,1{,}00245$$

With the values:

3 and 2 March	$H_o = 1098.32$	$H_{100} = 1491.02$
7 and 8 March	$H_o = 1098.33$	$H_{100} = 1491.00$
13 and 10 March	$H_o = 1098.34$	$H_{100} = 1491.05$

We find therefore (Comp. § 24):

3 and 2 March	$\alpha = 0{,}0036628$
7 and 8 March	$\alpha = 0{,}0036624$
13 and 10 March	$\alpha = 0{,}0036628$

while the mean of the three determinations is

$$\alpha = 0{,}0036627$$

Mr. CHAPPUIS was kind enough to send us a survey of the values obtained by him by means of the apparatus of the Bureau International [1]); they are the results of many and very carefully made determinations. Different apparatus for which the degree of precision was not the same were used for them.

In the large gas thermometer the relation $\frac{u}{V_o}$ (about 0.001) is more favourable than for the small one (0.003); measurements of the pressures in the former were much more accurate.

With the large gas thermometer for an initial pressure of 1000 m.m. he found in

1887	platinumiridium reservoir of 1 Liter	0,00366225—0,00366271
	in 7 determinations, mean	0,00366254
1889	platinumiridium reservoir	0,00366286—0,00366307
	in 4 determinations, mean	0,00366296
1895	reservoir of „verre dur"	0,00366201—0,00366224
	in 5 determinations, mean	0,00366217

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[1]) M. PERNET, who made the first experiments with the hydrogen thermometer at the Bureau International found 1884: 0.0036654 at 914mm. initial pressure
0.0036652 at 955mm. " "

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These observations relate to three different fillings. The mutual deviations in our determinations with a small transportable apparatus constructed especially with a view to the measurement of very low temperatures appear not to be larger than those in CHAPPUIS' results. Also the deviation of our mean value from that of CHAPPUIS is within the limits of deviation of his determinations with the large thermometer. We give here in addition the observations with CHAPPUIS' smaller apparatus:

1890 reservoir of „verre dur"	0,0036616—0,0036645
1st filling, 7 determination, mean	0,0036629
1890 2nd filling,	0,0036630—0,0036642
in 4 determination, mean	0,0036638

and the observations with the slightly varied initial pressure of 788 m. m.

1894 reservoir of „verre dur"	0,0036624—0,0036638
in 6 determination, mean	0,0036628
1894 reservoir of „verre dur",	0,0036621—0,0036626
mean	0,0036624

As could be expected larger deviations were found with this than in the determinations with the larger apparatus, in which the utmost accuracy was the chief object.

Physics. — Dr. E. VAN EVERDINGEN JR., "*On the* HALL-*effect and the resistance of crystals of bismuth within and without the magnetic field*". (Communication N°. 61 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

1. In crystals of bismuth it is not possible to give one definite value to the HALL-coefficient or to the increase of the resistance in the magnetic field; on the contrary these quantities depend to a considerable extent on the position of the principal crystallographic axis with respect to the lines of magnetic force and the direction of the current. This follows from my measurements, published in the Proceedings of April 21, 1897, p. 494 and June 26, 1897,

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p. 68 [1]). One of the hypotheses, introduced in order to explain the observed phenomena, amounted to this, that *no* increase of resistance would occur in the direction of the magnetisation. It would however have been sufficient to suppose, that the increase of resistance is *smaller* in the direction of the magnetisation than in the transverse directions. In order to allow of a decision between these suppositions, the increase of the resistance of the bars of bismuth N°. 1, 2 and 3 from the crystalline piece of bismuth from MERCK [2]) formerly mentioned, were measured once more while they were placed in the magnetic field with their longest dimension in the direction of the lines of force.

The results obtained with these bars made it appear most desirable to repeat the experiments with other and if possible better crystalline material. The remarkable results obtained by Mr. F. LOUIS PERROT at Genève for the thermo-electric constants of crystalline bismuth [3]) induced me to communicate with him. With extraordinary kindness he has put at my disposal one of the prisms of bismuth [4]) cut by himself with great care from a block of slowly cooled bismuth, for which assistance I take this opportunity of expressing my best thanks.

The complete results of the investigation on resistance, increase of resistance and HALL-effect in the bars cut from this prism I hope soon to publish; at present I wish to communicate separately a new particularity with respect to the HALL-effect which occurred during this work.

2. The observations lead to the following conclusion:

A bar of bismuth cut at right angles to the principal crystallographic axis, shows, in a magnetic field of about 5000 C. G. S. units *when placed with the principal axis* $\perp$ *the lines of force, a* HALL-*coefficient of normal magnitude and negative sign* (normal)*; when placed with the principal axis* $\parallel$ *the lines of force, a smaller*, **positive** HALL-*coefficient.*

Hence the same bar of bismuth which in one position shows a HALL-effect similar to nickel for instance, after having been turned through 90° about the direction of its longest dimension, shows a HALL-effect similar to tellurium and antimonium.

The positions of the various bars before they were cut from the crystal is shown in fig. 1 (2 $\times$ nat. size).

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[1]) Comm. Phys. Lab. Leiden, N°. 37, p. 7, N°. 40, p. 3.

[2]) Versl. d. Verg. 21 April 1897, p. 500. Comm. N°. 37, p. 16.

[3]) Arch. d. Sc. phys. et nat. (4) 6 p. 105 and 229, 1898, 7 p. 149, 1899.

[4]) Arch. d. Sc. phys. et nat. (4) 6 p. 121, 1898, Prism A.

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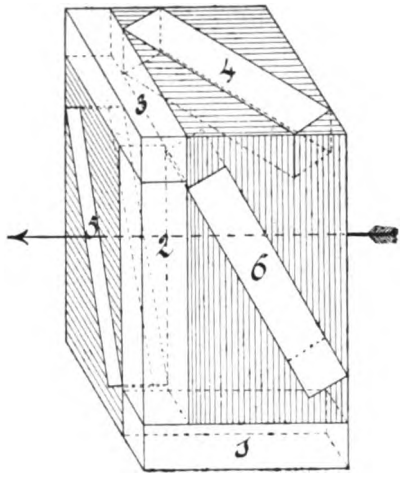

Fig. 1.

The principal axis, derived by PERROT from the position of the cleavage planes and characterised by the thermo-electric properties is indicated by an arrow. The bars 1, 2 and 3 have been cut along the three edges; 4, 5 and 6 with their longest dimension still parallel to one of the sides, but at angles of 30° or 60° to the edges of that side. If the crystal were completely homogeneous, No. 2, 3 and 5 fulfill the condition of being cut perpendicularly to the principal axis and ought to obey the rule given above.

The table below gives the results for the HALL-coefficient in two magnetic fields for each of the bars in 4 positions, always with the longest dimension perpendicular to the lines of force, but differing by consecutive rotation through 90° about that longest dimension. The numbers united by brackets refer to positions differing by 180°; in accordance with PERROT we indicate the positions in which the principal axis is perpendicular to the lines of force bij $\perp$, the other positions by $\parallel$.

HALL-coefficient R.

	$\perp$		$\parallel$	
N°.	MAGNETIC FIELD.			
	5000	2900	5000	2900
2	$\left\{\begin{matrix}-9.2\\-9.9\end{matrix}\right.$	$\left\{\begin{matrix}-11.0\\-11.9\end{matrix}\right.$	$\left\{\begin{matrix}-0.15\\-0.23\end{matrix}\right.$	$\left\{\begin{matrix}-0.70\\-0.51\end{matrix}\right.$
3	$\left\{\begin{matrix}-8.0\\-7.9\end{matrix}\right.$	$\left\{\begin{matrix}-10.1\\-10.2\end{matrix}\right.$	$\left\{\begin{matrix}\underline{+0.16}\\-0.18\end{matrix}\right.$	$\left\{\begin{matrix}-0.10\\-0.56\end{matrix}\right.$
5	$\left\{\begin{matrix}-7.5\\-7.4\end{matrix}\right.$	$\left\{\begin{matrix}-9.7\\-9.6\end{matrix}\right.$	$\left\{\begin{matrix}\underline{+0.58}\\\underline{+0.56}\end{matrix}\right.$	$\left\{\begin{matrix}\underline{+0.36}\\\underline{+0.19}\end{matrix}\right.$

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A single view of the vertical columns and the corresponding positions $\perp$ and $\parallel$ in a horizontal row is sufficient to carry the conviction, that the above mentioned relation of the HALL-coefficient to the position of the principal axis with respect to the lines of magnetic force not only is confirmed, but is even more marked than was found before. The new rule however, so far as the positive sign is concerned, is not satisfied in one position of 3 and in both positions of 2. The following remarks indicate why I nevertheless regard the results with 5 as normal.

1°. No certainty exists as to whether the original crystal was perfectly homogeneous, though it is certainly the most regular piece of bismuth ever tested for HALL-effect. PERROT himself admits the possibility that small irregularities, „macles" are present. If this be the case they are very probably most important at the edges, and hence particularly in the bars 2 and 3. The rather large discrepancy in bar 2 between the bracketed values indicates that this especially cannot have been quite homogeneous. Taking for granted that the rule given at the head of this § holds, irregularities can only alter the HALL-coefficient by a negative quantity in the position $\parallel$, and it would not require many to make that coefficient change sign altogether.

2°. Considering that a rotation of 90° at all events considerably alters the HALL-coefficient, the position of the bars would of course require to be regulated very accurately in order to exclude errors. With bars of about 3 mm. thickness it will not be astonishing that this accuracy was not attained. Here as well as with the first source of errors only diminution of a positive coefficient or even change into a negative one is to be expected. I suspect that this cause occurred with 3, the more so because in an experiment made some months ago in the first position $\parallel$ we also found a positive value but smaller than 0.16. On the contrary the value + 0.58 for 5 is a mean of values + 0.57 and + 0.59 obtained in rapid succession.

The observations further agree in this that a decrease in the magnetic field always causes a variation of the HALL-coefficient in the position $\parallel$ with a comparatively very large negative value. This gave rise to the supposition that the reversal of sign observed with 3 between 5000 and 2900 might occur with the other bars between other limits. With 2 this remains to be tested, but requires stronger fields. With 5 however in the first position $\parallel$ in a magnetic field

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of about 1300 C.G.S. —0.06, in the other position about 0 was really found, so that the supposition was here confirmed.

I am unaware of any disturbances which might cause an *apparent* positive HALL-coefficient in the method used by me. Only if the galvano-magnetic difference of temperature should rise here to an appreciable value much faster than usually, for instance in one second, it might have an influence to that effect. During the experiments there was no sign of this, and I consider such a disturbance to be quite improbable.

3. Certainly it will not be easy to give an explanation of these variations based upon the electron-theory. It seems however to me as if the reversal of sign need not represent a special difficulty, particularly because the theory had to reckon already with reversal by other influences. We take as an example the simplest theory which assumes the HALL-effect to be proportional to the difference of the migration-velocities $(u—v)$. Usually in order to explain the phenomena in bismuth it is assumed that v is especially important, which constitutes an analogy with cathodic rays and the ZEEMAN effect. Hence in order to get a considerable variation of the HALL-coefficient it is certainly necessary to decrease v considerably. If this is carried far enough a reversal of sign of $u—v$ may be expected. Should the objection be made that u here appears to be a non-negligible quantity, I can only remark that the positive value obtained for D (rotation of equipotential lines) for bismuth is even smaller than that for antimony and tellurium: and hence this does not constitute a *new* difficulty.

Reversal of sign was observed in consequence of:

a. Variation of temperature, with nickel, by CLOUGH and HALL [1]).

b. Variation of magnetic field, with alloys of bismuth with 1—6 pCt. of tin, by v. ETTINGSHAUSEN and NERNST [2]); with impure bismuth, by BEATTIE [3]).

c. Addition of an other metal in a constant field with bismuth mixed with increasing quantities of tin, by v. ETTINGSHAUSEN and NERNST [2]).

To this we can add now as fourth cause:

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[1]) Proc. Amer. Acad. 20 p. 189, 1893.

[2]) Wied. Ann. 33 p. 474, 1888.

[3]) TRANS. R. Soc. Edinb. 38(1) p. 225, 241, 1896.

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d. Variation of position with respect to lines of magnetic force, in crystals of bismuth.

As mentioned before, in our experiments *b* also occurred.

In conclusion we note the fact, that increase of magnetic field *always* alters the HALL-coefficient by a *positive* amount, which seems to indicate that the influence of this increase is felt especially in *v* [1]).

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[1]) See § 6 Communication N°. 58, Versl. Kon. Akad. v. Wetensch. 30 Juni 1900, p. 195, Comm. N°. 58, p. 23.

(October 24, 1900.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday October 27, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 October 1900 Dl. IX).

CONTENTS: "On the pedal circles of the point-field in reference to a given triangle." By Prof. JAN DE VRIES, p. 323. — "Experimental determination of the Limiting Heat of Solution." By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 327. — "Contributions to the knowledge of some undescribed or imperfectly known fungi" (3rd Part). By Prof. C. A. J. A. OUDEMANS, p. 332. — "On the MACMAHON genelarization of the NEWTON-GIRARD formulae." By Prof. L. GEGENBAUER (Communicated by Prof. JAN DE VRIES), p. 347. — "On different forms of hereditary variation of microbes." By Prof. M. W. BEIJERINCK, p. 352. — "On the development of Buds and Bud-variations in Cytisus adami." By Prof. M. W. BEIJERINCK, p. 365. — "On the permeability of the red bloodcorpuscles for NO_3- and SO_4-ions". By Dr. H. J. HAMBURGER, p. 371. — Erratum p. 374.

The following papers were read:

Mathematics. — "*On the pedal circles of the point-field in reference to a given triangle.*" By Prof. JAN DE VRIES.

(Read September 29, 1900)

1. If P_1, P_2, P_3 are the orthogonal projections of the point P on the sides of the triangle $A_1 A_2 A_3$, the circle π passing through P_1, P_2, P_3 is called the pedal circle of P.

If π intersects the sides of the triangle for the second time in P_1', P_2', P_3', these three points are the projections of the point P' isogonally conjugated to P, i.e. the angles $A_k A_l P$ and $P' A_l A_m$ are

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equal. In other words, P and P' are the real foci of a conic inscribed in the triangle $A_1 A_2 A_3$.

So each circle π belongs to two points P. These points coincide for each of the four circles touching the sides.

The point P being situated on the circumscribed circle $A_1 A_2 A_3$, the circle π degenerates into the right line p of WALLACE (SIMSON) belonging to P and the right line at infinity; P is the focus of a parabola inscribed in $A_1 A_2 A_3$. The right lines p envelop the well-known tricuspidal hypocycloid, discovered by STEINER, for which curve of the third class the right line at infinity is the isolated double tangent.

2. Through two points P_1 and P_2, lying respectively on $a_1 \equiv A_2 A_3$ and $a_2 \equiv A_1 A_3$, three circles π pass. In the first place of course the pedal circle of the point P of which P_1 and P_2 are two projections. If a point Q describes the right line l_1 cutting a_1 orthogonally in P_1, the locus of the isogonally conjugated point Q' is a conic A_1 through A_1, A_2, A_3. With the right line l_2 cutting a_2 orthogonally in P_2 this parabola has two points Q' and R' in common, of which the isogonally conjugated points Q and R lie on l_1. Evidently the common pedal circle of Q and Q' passes through P_1 and P_2; in like way these two points lie on the circle π belonging to R and R'.

If we take P_2 at infinity, these three circles degenerate into the three right lines of WALLACE meeting in P_1.

3. The locus of the pairs of points P, P' collinear with a given point M is a cubic $\mu^{(3)}$, generated by the pencil of rays (M) and the projective pencil of the conics isogonally conjugated to those rays. Evidently this curve passes through the vertices A_1, A_2, A_3 and through the double points of the correspondence, i. e. the centres I of the four circles touching the sides. If M is to be the mid-point of two conjugated points P, P', then the point harmonically separated by P, P' from M must lie at infinity; so it must be one of the points of intersection of the right line r_∞ with the polar conic of M with respect to $\mu^{(3)}$. Now this conic passing through the four points I is an orthogonal hyperbola; consequently we can draw through M two lines normal to each other, each of which contains a pair P, P'.

But one of those pairs is imaginary. For, a conic touching the three right lines $A_k A_l$ is entirely determined if its centre M is known; so of the two pairs mentioned above one consists of the real, the other of the imaginary foci of the conic.

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For the ellipse $a^2 y^2 + b^2 x^2 = a^2 b^2$ the pedal curve of the real foci is the circle $x^2 + y^2 = a^2$; the projections of the imaginary foci $x = 0, y = \pm c i$ on the tangents lie in the circle $x^2 + y^2 = b^2$.

Evidently this second circle becomes imaginary for the hyperbola; it becomes a point circle at infinity for the parabola. For the curves of the second class, of which the tangents form two pencils of rays, the circle $x^2 + y^2 = b^2$ degenerates into a point as well. For, the tangential equation $a^2u^2+b^2v^2=1$ of the ellipse is transformed into the equation of the pair of points $x = \pm a, y = 0$, if b is made equal to zero.

4. By what precedes is proved that each point of the plane Φ in which the triangle $A_1 A_2 A_3$ lies, is the centre of two circles π. If, following FIEDLER, we represent each circle π by its two poles on the sphere of which π is a main circle, we obtain as representating surface of the system (π) a surface $\mu^{(4)}$ of order four placed symmetrically with respect to Φ.

With the aid of $\mu^{(4)}$ we can easily show that any two points S_1 and S_2 taken arbitrarily lie on *three* circles π.

For, the circles through S_1 and S_2 are represented by an orthogonal hyperbola $\gamma^{(2)}$ of which the plane bisects the right line $S_1 S_2$ orthogonally, the asymptotes intersecting the plane Φ at angles of 45°. Now the points of contact of the asymptotes are to be regarded as images of the only tangent of the previously named hypocycloid having the direction of $S_1 S_2$. The remaining six points of intersection of $\gamma^{(2)}$ and $\mu^{(4)}$ originate from three circles π.

5. However, three pairs of points can be indicated each of which lie on an infinite number of circles π. For, if P is a point of $A_2 A_3$, its pedal circle passes through A_1 and the projection B_1 of A_1 on $A_2 A_3$. From this follows that the plane γ_1, intersecting Φ orthogonally in the line connecting the mid-points C_3 and C_2 of $A_1 A_2$ and $A_1 A_3$, contains an orthogonal hyperbola situated entirely on $\mu^{(4)}$.

This plane touches $\mu^{(4)}$ along the right line $C_2 C_3$. For each point of this line must be regarded as the centre of a degenerated curve of the second class.

So the intersection of $\mu^{(4)}$ and Φ consists of four right lines, i. e. the lines $C_k C_l$ and the right line at infinity.

The lines $C_1 C_2$, $C_2 C_3$, $C_3 C_1$ divide the plane Φ into seven parts. If M lies inside the triangle $C_1 C_2 C_3$ or in one of the angles formed by producing two sides, then the corresponding conic is an ellipse and M accordingly the projection of four real points of the represen-

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tating surface. If on the contrary M belongs to one of the parts of Φ limited by a side and the productions of the two other sides, the conic is an hyperbola, so that M determines but *one* real circle π and is consequently the projection of two real points of $\mu^{(4)}$.

So in each of the "elliptic cases" formed by the planes $\gamma_1, \gamma_2, \gamma_3$ lies a sheet of $\mu^{(4)}$, intersecting Φ orthogonally in three right lines and possessing a singular point in the two images of one of the points I.

The four sheets coincide in the six nodes, which are situated in C_1, C_2, C_3, and on $C_1 C_2$, $C_2 C_3$, $C_3 C_1$ at infinity.

The "hyperbolic" parts of $\mu^{(4)}$ pass into the "elliptic" parts along the hyperbolae situated in the tangent planes γ_k.

The plane, bisecting orthogonally an angle of the given triangle or its supplement, containing four nodes, intersects $\mu^{(4)}$ according to two conics meeting Φ on the right lines $C_k C_l$ and at infinity. Consequently one of these conics is a parabola, whilst the other one must be an orthogonal hyperbola, because its points at infinity are the images of the right line of WALLACE perpendicular to the plane of division.

6. The circles π, passing through a point D and touching a right line l, are represented by two parabolae, of which the planes form with Φ angles of 45°. They have four points at infinity in common with $\mu^{(4)}$; the remaining points of intersection indicate six circles.

This result is found back by searching for the coincidences of the correspondence (3, 3) which is determined on l by the circles π containing D.

The circles touching two right lines l and m are represented by four right lines; these determine on $\mu^{(4)}$ the images of eight circles π having l and m as tangents.

If l and m coincide with two sides of the triangle $A_1 A_2 A_3$, the eight circles coincide two by two in the four inscribed circles.

Prof. SCHOUTE draws attention to the fact, that the surface investigated by the speaker may be called "wave surface of the inscribed conics", the cyclographic representation demanding simply that on the perpendicular to the plane in point M we take on either side points, the distances of which to the plane are equal to the two axes of the inscribed conic having M as centre. The nodes corresponding with the inscribed- and escribed circles are the points of "conical refraction".

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The equation of the indicated surface is

$$(ax + by + cz)\,(by + cz - ax)\,(cz + ax - by)\,(ax + by - cz)$$
$$- 16\,(x^2 \sin 2A + y^2 \sin 2B + z^2 \sin 2C)\,I R^2 u^2 + 16 I^2 u^4 = 0,$$

if x, y, z are the usual trilinear coordinates, u denotes the distance from the point to the plane of the triangle and a, b, c, A, B, C, I, R indicate as usual the sides, the angles, the area and the radius of the circumscribed circle of triangle ABC.

Chemistry. — "*Experimental Determination of the Limiting Heat of Solution*" (First Part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read September 29, 1900.)

1. When a substance is dissolved in any medium a quantity of heat appears which is generally called the "heat of solution".

It has been shown, particularly by VAN DEVENTER and VAN DE STADT [1]), that this universal name may easily lead to confusion. They point out that a precise definition is necessary as the quantity of heat which is generated (for instance, when dissolving a salt in water) depends on the amount of substance already present in the solvent.

If equal quantities of a salt are successively introduced into pure water each quantity on dissolving will produce a different heat effect so that there really exists an unlimited number of different heats of solution which each depend on the concentration of the liquid into which the new quantity of the salt is introduced.

If a certain quantity of a salt is dissolved in a large amount of water so that the solution is so dilute, that on further dilution no heat is evolved, the heat effect accompanying the dissolving is called (by V. DEVENTER and V. D. STADT) the "*first heat of solution*" (calculated on 1 gram-molecule of salt) This is the quantity which is generally called the "*heat of solution*" and which has been determined for a large number of substances by BERTHELOT, THOMSEN and others.

This heat of solution is also called "*heat of solution in much water*" or "*heat of solution to extreme dilution*".

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[1]) Zeitschrift für phys. Chemie, 9. 34 (1892).

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As the quantity of heat evolved during dissolution, depends on the concentration of the liquid employed, each fresh quantity of salt will cause a different heat effect until the solution has become saturated.

Each of these heats of solution excepting the last, is called an "*intermediate*" heat of solution. The sum of the *intermediate* heats of solution is called the "*integral*" or "*total*" heat of solution or also "*heat of solution to saturation*".

2. The last term of the integral heat of solution is particularly important theoretically. It represents the quantity of heat evolved when a salt (calculated per gram molecule) dissolves in its own saturated solution.

This quantity of heat is called "*fictitious*", *theoretical* or *ideal* heat of solution also "*last or limiting heat of solution*". It is this factor which plays a great part in the thermodynamics of solutions; we refer to the expressions given by V. D. WAALS [1]), VAN 'T HOFF [2]), LE CHATELIER [3]) and BAKHUIS ROOZEBOOM [4]) for the relation between the solubility and temperature.

LE CHATELIER and BAKHUIS ROOZEBOOM already pointed out and REICHER and VAN DEVENTER demonstrated experimentally that there can exist a great difference between the first and the limiting heat of solution and that they may even have a different sign [5]).

That these quantities coincide in the case of substances which are but little soluble, will be easily understood.

3. Only the „first heat of solution" is accessible to determination by a direct calorimetric method. The other heats of solution may be calculated from the heats of dilution, by means of HESS' law, then from the table of the heats of dilution of solutions of different concentrations and from the first heat of solution the heat effect may be calculated with which increasing quantities of salt dissolve in a definite volume of water, and from this the heat of solution of the last quantity may be obtained by extrapolation.

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[1]) Zittingsversl. Kon. Akad. van Wetensch., 28 Febr. 1885.

[2]) VAN 'T HOFF, Lois de l'Equilibre chimique etc. Kongl. Svenska Vetenskaps Akad. Handl. 21. 17 (1886). OSTWALD's-Klassiker 110. Translation by BREDIG, S. 55.

[3]) Recherches expérimentales et théoriques sur les équilibres chimiques. Extrait des Annales des Mines, livraison Mars—Avril 1888, p. 138. (Paris, DUNOD).

[4]) Rec. des Trav. chim. des Pays-Bas 8, 123, (1889).

[5]) Zeitschrift für. phys. Chemie 5, 559 (1890).

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It will be easily seen that the accuracy of such a calculation will leave much to be desired and this is why, thus far, the limiting heat of solution is but approximately known in a few instances.

4. I now wish to describe two methods for the determination of the limiting heat of solution which do not differ in principle although at present for certain experimental reasons the second method is preferable to the first.

In both cases, two electrical measurements and a calorimetric one (which in many cases has already been executed by BERTHELOT or THOMSEN) lead to the knowledge of the desired heat factor which we will call L_f.

5. In order to be better understood we will choose a definite example and make it our object to determine the limiting heat of solution (L_f) of $AgNO_3$ say at $t°$.

FIRST METHOD.

We construct a galvanic cell according to the following scheme:

Ag.	Solution of $AgNO_3$ saturated at $t°$ C.	Very dilute solution of $AgNO_3$.	Ag.

In view of the future determination of the temperature-coefficient of the cell, the solid phase will *not* be introduced into the saturated solution but a clear saturated solution will be employed.

The mechanism of this cell during the passage of the current is now, according to known principles, as follows:

When one gram-ion of silver dissolves in the weak solution, the concentration of silver in that solution is increased by 1 gram-ion; but at the same time, if $(1-n_1)$ is the migration constant of the silver, $(1-n_1)$ gram-ions of silver will have passed from the dilute into the saturated solution.

The increase in the dilute solution therefore amounts to n_1 gram-ions.

The saturated solution has, of course, become correspondingly poorer in silver.

At the same the NO_3-ions have been displaced in the opposite direction. If n_1 is their migration constant, then n_1 gram-ions of NO_3 have passed from the saturated to the diluted solution, therefore, during the passage of 96540 Coulombs, n_1 gram-ions of Ag and n_1

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gram-ions of NO_3 have been transferred from the saturated to the dilute solution.

6. As the cell described is a reversible one we may apply the equation of GIBBS and VON HELMHOLTZ.

$$E_e = \frac{E_c}{n\varepsilon_o} + T\frac{dE}{dT}.$$

As n is here $= 1$ we get:

$$E_c = \varepsilon_o\left(E_e - T\frac{dE}{dT}\right).$$

We may imagine the heat effect of the change which takes place in the cell during the passage of 96540 Coulombs as occurring in two stages:

1st. Withdrawal of n_1 $AgNO_3$ from the solution saturated at $t°$; heat effect $-n_1 L_f$.

2nd. Solution of n_1 $AgNO_3$ in the extremely dilute solution; heat effect $n_1 W_1$ (representing by W_1 the first heat of solution).

We thus get:

$$E_c = \varepsilon_o\left(E_e - T\frac{dE}{dT}\right) = -n_1 L_f + n_1 W_1$$

or

$$L_f = W_1 - \frac{\varepsilon_o}{n_1}\left(E_e - T\frac{dE}{dT}\right).$$

If now the E.M.F. of the cell is determined at $t°$ and also the temperature coefficient at that temperature, then all the quantities on the right hand side of the equation are known and consequently L_f, which we desired to determine.

7. A single remark remains to be made: the dilute solution must be so chosen that W_1 is really practically the first heat of solution. If it is made too dilute, the accuracy with which E and $\frac{dE}{dT}$ can be determined (for instance by POGGENDORFF's compensation method) becomes too small as the resistance would become unduly great. At the same time any (small) heat of dilution would be

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neglected. It is therefore, in any case as well to keep within certain limits [1]).

It is, of course, obvious that as a rule, electrodes which are reversible in regard to the anion may also be employed. This method is not likely to be used at present because the migration constants in concentrated solutions and their dependance on the temperature have been studied so little n_1 for saturated solutions of $AgNO_3$ being quite unknown.

SECOND METHOD.

8. This method which, as already explained, quite corresponds in principle with the first one, is capable of being realised experimentally.

We take for instance the case that the limiting heat of solution of thallous sulphate is to be determined and construct a cell according to the following scheme:

$$\begin{array}{c|c|c} Hg \\ Hg_2SO_4 & \text{Solution of } Tl_2SO_4 \text{ saturated at } t^\circ \text{ C.} & Tl \end{array}$$

connected in opposition to:

$$\begin{array}{c|c|c} Hg \\ Hg_2SO_4 & \text{Very dilute solution of } Tl_2SO_4 & Tl. \end{array}$$

When 2×96540 Coulombs have passed through this combination, 1 gram-molecule of Tl_2SO_4 has been transferred from the saturated to the dilute solution.

In the equation

$$E_e = \frac{E_c}{n\varepsilon_o} + T\frac{dE}{dT}$$

$n = 2$ therefore

$$E_c = 2\,\varepsilon_o\left(E_e - T\,\frac{dE}{dT}\right),$$

---

[1]) When the saturated and the diluted solutions differ very much in degree of dissociation, there will exist a difference between the ionisation-heats at the electrodes in those solutions. Provisionally, we only know that difference will be very small. Still, a numerical determination would be interesting, in which OSTWALD's equation (Zeitschr. f. phys. Chemie 11, 501, 1893) might be a guide.

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whilst further

$$E_c = - L_f + W_1 ,$$

in which L_f represents the limiting heat of solution and W_1 the first heat of solution of Tl_2SO_4, therefore:

$$- L_f + W_1 = 2\,\varepsilon_o \left(E_e - T\frac{dE}{dT} \right)$$

or

$$L_f = W_1 - 2\,\varepsilon_o \left(E_e - T\frac{dE}{dT} \right).$$

The right hand side of the equation contains again only known quantities if the E.M.F. of the cell and its temperature coefficient at $T°$ have been determined. W_1 may be borrowed from the table of BERTHELOT or THOMSEN [1]).

The advantage of this method over the first lies in the fact that migration is excluded here and that we therefore, avoid the difficulty that the migration constants of concentrated solutions are not known.

I hope to describe the measurements in a future communication.

Amsterdam, Chem. University Lab., Aug. 1900.

Botanics. — "*Contributions to the knowledge of some undescribed or imperfectly known Fungi*" (3rd Part) [2]). By Prof. C. A. J. A. OUDEMANS.

56. ASCOCHYTA RHEI Ellis et Everhart, Proc. Acad. Sc. Philad. 1893, p. 160 (= Phyllosticta Rhei Ell. Ev. ante annum 1893); Sacc. Syll. XI, 525, forma *caulincola* Oud. — On the stem and branches of *Rheum Rhaponticum*. — Nunspeet, Oct. 2, 1899; Mr. BEINS.

Maculae nunc nigrescentes, tunc vero pallescentes, irregulariter limitatae. Perithecia numerosissima, congesta, $^1/_{10}$—$^1/_8$ mill. in diam., epidermide velata, depressa, membranacea, vertice perforata. Sporulae hyalinae, cylindraceae, ad polos rotundatae, biloculares, non aut vix constrictae, 7—14 × 3.5—4 μ.

57. ASCOCHYTA PSAMMAE Oud. n. sp. — On the leaves of *Psamma littoralis* (= Calamagrostis arenaria = Ammophila arundinacea = Psamma arenaria). — Dunes of Scheveningen, Sept. 1891.

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[1]) See note on pag. 331. The same remarks also apply here.

[2]) For 2nd Part see these Proceedings p. 230.

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Perithecia epiphylla, sparsa vel laxe-caespitosa, epidermide velata, non autem immersa, lenticulari-depressa, membranacea, mollia, nigra, in luce pervia autem pallide-fusca, $^1/_8$ mill. in diam., vertice perforata. Sporulae oblongae, dilute fuscescentes, biloculares, ad polos anguste-rotundatae, sine constrictionis vestigio, eguttulatae, $11^2/_3$—$14 \times 4^2/_3$ μ.

Our fungus must by no means be confounded with *Ascochyta perforans* Sacc. (Syll. III. 406) or, what according to this author would be the same, with *Sphaeria perforans* Roberge (Desm. Ann. Sc. nat. 2, XIX, 357 and Desm. Exs. 1st Series, 1st Ed., 1843, N°. 1288), because under this number, in the copy which I possess of this rare work, there are found Psamma-leaves, but no perithecia whose spores correspond with those of Ascochyta. They are indeed bilocular and uncoloured, but each extremity bears a sickle-shaped appendix, whose convex side is turned upward, and besides shows two inwardly curved ends and, in the middle, a short, thick stalk, by which it is joined to the summit of the spore. Perithecia with such spores can only belong to the genus *Darluca*, provided its character be somewhat expanded and, besides the presence of short-triangular or thread-shaped, there be also allowed comb-shaped, jelly-like appendices at the extremities of the spores. In this case the new form found by me might be denominated *Darluca cristigera*. These comb-bearing spores are, exclusive of the appendices, 25—26 μ long, and 14 μ wide, a measurement mentioned by DESMAZIÈRES, not however taken over by SACCARDO, but which is in any case much more considerable than was ever found in an *Ascochyta*. A slight deviation, in SACCARDO's description, when compared to that of DESMAZIÈRES, is found in so far as the former calls the spores at one and the same time "ellipticae" and "acutiusculae", notwithstanding these terms seem to exclude each other, and the second of the two is not found in the latter author.

In his diagnosis of *Ascochyta perforans* (Syll. III, 406) SACCARDO also refers the reader to the article on *Sphaerella perforans* (Desm.) Sacc. in Vol I, p. 538 of the Sylloge, still, it cannot escape the attention of those who attend to this reference, that by this *Sphaerella* there is meant nothing else but the *Sphaeria perforans* already discussed by us, and the same number in SACCARDO's herbarium venale. DESMAZIÈRES' silence about the existence of asci induced SACCARDO to doubt of the justness of the name of "Sphaeria", changed by himself, in accordance with the more recent ideas, into "Sphaerella". And herein the Italian Professor is right. Follows however that *Sphaerella perforans* has no right of existence any more and

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can have no meaning but as a synonyme of *Darluca cristigera*.

Remains the question whether our fungus might perhaps belong to *Ascochyta graminicola* Sacc. (Mich. I, 127 and Syll. III, 407). The answer, however, we think, can be only negative, for though both species correspond in many respects with each other, still a nearer investigation proves that *Asc. graminicola* has ovoid-fusiform, bicellular spores, whilst in *Asc. Psammae* are found oblong spores without drops. — *Ascochyta graminicola* var. *Holci* and *Asc. graminicola* var. *ciliolata* Sacc. (both referred to on pag. 407 Vol. III of the Syll.) may remain out of consideration, the former having large four-dropped spores, the latter, on account of the gelatinous filaments at the summits of those organs, being obliged to withdraw to the genus *Darluca-Ascochyta graminicola* Sacc. var. *Brachypodii* Trail. (Sacc. Syll. X, 308) comes not into consideration, its spores being too large ($15-17 \times 5\ \mu$) and somewhat crooked; *Asc. graminicola* var. *Caeruleae* not, as here again the spores bear appendices and accordingly belong to Darluca; lastly, neither *Asc. graminicola* var. *leptospora* (Sacc. Syll. XI, 308), as the spores are too narrow, as may be inferred from the name of the variety ($\lambda\acute{\epsilon}\pi\tau o\varsigma$ = slender).

So, we think ourself authorised to maintain the name of *Ascochyta Psammae*, and further, to withdraw the species *Ascochyta perforans* with their synonymes: *Sphaeria perforans* and *Sphaerella perforans*, together with *Ascochyta graminicola* var. *ciliolata* and *Ascochyta graminicola* var. *Caeruleae*, from the genera to which they hitherto belonged, bring them over to *Darluca*.

58. ASCOCHYTA SOLANICOLA Oud. n. sp. — On the leaves of *Solanum nigrum*. — Nunspeet, Oct. 11, 1898; Mr. BEINS

Maculae orbiculares (mill. 5 in diam.) sive ellipticae (18×15 mill.), numerosae, fuscescentes, linea saturatius tincta in pagina superiore circumscriptae, pallide virescentes in pagina inferiore, vulgo steriles, denique aridae, fragillimae, foramen circulare vel ellipticum post destructionem relinquentes. Perithecia epiphylla, sparsa, $^1/_5$ mill. in diam., fusca, prominentia, primo epidermide velata, denique exposita, vertice perforata. Sporulae bacillares, ad polos rotundatae, hyalinae, biloculares, sine constrictionis vestigio, $10-12 \times 2^1/_2\ \mu$.

Ascochyta solanicola is distinguished from *Asc. Solani* Oud. (Ned. Kruidk. Arch. 2, VI, 44; Sacc. Syll. X, 304), on the stems of Solanum tuberosum, by the absence of black filaments at the base of the perithecia, and by the smaller spores ($10-12 \times 2^1/_2\ \mu$ to $14 \times 7\ \mu$); from *Asc. Lycopersici* Brunaud (Sacc. Syll. X, 304), on the leaves of Lycopersicum esculentum, by the brown, not black perithecia, by

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the want of the slightest constriction on the height of the partition, and by longer spores (10—12×2$^1/_3$ μ to 8—10×2$^1/_2$ μ); from *Asc. socia* Pass. (Sacc. Syll. X, 304), on the leaves of Lycopersicum esculentum, by the somewhat longer and somewhat shorter spores (10—12 ×2$^1/_3$ μ to 8—10×2$^1/_2$—3 μ); from *Asc. Atropae* Bresadola (Hedw. XXXII, 1893, p. 32 and Sacc. Syll. XI, 524), on the leaves of Atropa Belladonna, by the much larger perithecia ((200 μ to 70—80 μ) and the narrower spores (10—12×2$^1/_3$ μ to 8—12×4 μ); from *Asc. Daturae* Sacc. (Mich. I, 163 and Syll. III, 402), on the leaves of Datura Stramonium and arboreum, by the larger perithecia (200 μ to 100 μ), otherwise coloured dots, and longer but narrower spores (10—12×2$^1/_3$ μ to 7—8×3 μ); from *Asc. Nicotianae* Pass. (Sacc. Syll. III, 401), on the leaves of Nicotiana Tabacum, by the absence of the slightest constriction on the height of the partition and of fine granules in the protoplasm; lastly, from *Asc. physalina* Sacc. (Mich. I, 93 and Syll. II, 401), on the leaves of Physalis Alkekengi, by the much smaller spores (10—12×2$^1/_3$ μ to 25—28×8 μ) and the absence of vacuoles in the protoplasm.

*Ascochyta Tussilaginis Oud. n. sp. — On the leaves of *Tussilago Farfara*. Apeldoorn, Oct. 6, 1897. — Cf. Ned. Kr. Arch. 3, I, 498, et Hedw. XXXVII, 178.

59. Ascochyta viburnicola Oud. n. sp. — On the branches of *Viburnum Opulus*, together with *Phoma viburnicola*. — Nunspeet, April 14, 1899; Mr. Beins.

Maculae nullae. Perithecia numerosa, parva, depressa, sub peridermate occultata, vertice perforata. Sporulae cylindraceae vel cylindraceo-fusiformes, ad polos rotundatae, rectae, solitariae hyalinae, in massam condensatae dilute-olivaceae, biloculares, 9$^1/_3$×2$^1/_2$ μ.

Differt ab *A. Viburni*, *A. Lantanae* et *A. Tini* sporularum dimensionibus, quippe quae exprimuntur numeris

10—12×3.5—4 μ pro *A. Viburni*.
11×2 μ pro *A. Lantanae*.
6—10×3 μ pro *A. Tini*.

CYTODIPLOSPORA Oudemans.

(Ned. Kruidk. Archief 2^e Serie, VI, 292).

The genus *Cytodiplospora* may be considered as to differ from *Cytospora* by bicellular spores.

Though Saccardo p. 523, Vol. XI of his Sylloge, rightly assigned

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a place to this genus among the Hyalodidymae, it was in Vol. XII of the said work (p. 162), elaborated by SYDOW, erroneously mentioned as belonging to the Phaeophragmeae, and in the "Index generalis Generum", in the back part of volume XIV, much to the detriment of the reader, an *s* is added to Cytodiplospora which is thereby changed into *Cystodiplospora.*

The first *Cytodiplospora* found by me, lived on branches of *Castanea vesca*, and was described by me under the name of *Cytodiplospora Castaneae* in Nederl. Kruidk. Archief, 2, VI, 528. A second species, found on Birch-branches, I mentioned under the title of *Cytodiplospora Betulae*, in Hedwigia XXXVII (1898) p. 317. A third species, found of late on branches of *Acer Pseudoplatanus* and *dasycarpum*, I here mention by the name of:

60. CYTODIPLOSPORA ACERUM Oud. n. sp. — On branches of *Acer Pseudoplatanus* and *Acer dasycarpum.* — Bussum, April, 1900. C. J. KONING.

Pustulae numerosae, irregulariter distributae, peridermate tectae, parum prominentes, sed praesentiam suam saepe jam ab initio tradentes macula subcutanea orbiculari vel annulari, nigra, opaca, 1 ad $1^1/_2$ mill. in diam. Peridermate rupto, stroma conspicuum fit depressum, fuliginosum, structura parenchymatica tenerrima insigne, intus lacunosum, i.e. septis pluribus flexuosis incompletis in loculamenta plurima variae dimensionis divisum. Sporulae numerosissimae, biloculares, fusiformes, rectae, hyalinae, ad polos anguste rotundatae, 12—14$\times$ $2^1/_3$—3 μ, non constrictae, basidiis brevibus suffultae.

DIPLODINA Westendorp.

61. DIPLODINA DASYCARPI Oud. n. sp. — On branches of *Acer dasycarpum.* — Scheveningen, May 1894.

Perithecia in caespites densos appropinquata, subcutanea, denique exposita, globuloso-papillata, nigra. Sporulae fusiformes, hyalinae, ad polos anguste rotundatae, biloculares, non constrictae, eguttulatae, 12$\times$$2^1/_2$ μ. — Differt a *D. Acerum* sporulis minus largis (12$\times$$2^1/_2$ μ contra 12—16$\times$4—4.5 μ) et sporulis ne minime quidem constrictis.

62. DIPLODINA NEGUNDINIS Oud. n. sp. — On branches of *Negundo fraxinifolia.* — Naarden, Febr. 1900; C. J. KONING.

Perithecia numerosissima, dense congesta, in parenchymate corticali leviter immersa, orbiculari-depressa, vertice tandem periderma laxe adhaerens perforantia, 100 μ in diam. Sporulae bacillares, ad polos

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rotundatae, continuae, hyalinae, biloculares, leviter in medio constrictae, nonnumquam imo panduriformes, 11—14×3—5 μ, eguttulatae, sporulis plurimis continuis, brevibus, phomiformibus (nondum penitus evolutis?) commixtae (Pl. IV, fig. 7).

THORACELLA n. g. Oudemans.

Stroma piceum, micans, infracuticulare, primo laeve, postea rugosum et foveolatum, e stratis duobus aequialtis composito: superiore pseudoparenchymatoso, fuliginoso, inferiore e hyphis intertextis pachydermatosis, hyalinis composito; conceptaculis sporularum in strato superiore effossis, primo absconditis, postremo ostiolo hiantibus. Sporulae fusiformes, ad polos acutiusculae, hyalinae, in medio 1-septatae, basidiis filiformibus suffultae.

63. THORACELLA LEDI Oud. n. sp. On the leaves of *Ledum palustre;* Nunspeet, Sept. 9, 1898; Mr. BEINS.

Stroma amphigenum, nunc partem tantum folii, tunc vere totum folium occupans, piceum, micans, primo laeve, postea rugosum et foveolatum, ex ostiolis conceptaculorum perforatis paululum prominentibus p. m. inaequali. Conceptacula p. m. numerosa. Sporulae fusiformes, hyalinae, 7—11 × 2 μ, ad polos acutiusculae, in medio 1-septatae, basidiis filiformibus longiusculis suffultae. — Saepe *Ascochyta Ledi* Oud. concomitata.

δ. Phragmosporae.

HENDERSONIA Berkeley.

*HENDERSONIA AGROPYRI REPENTIS Oud. n. sp. On the leaves of *Agropyrum repens.* Nunspeet, March 13, 1898; Mr. BEINS. Cf. Ned. Kr. Arch. 3, I, 500.

64. HENDERSONIA GROSSULARIAE Oud. n. sp. On the leaves of the young branches of *Ribes Grossularia.* — Apeldoorn, May 19, 1897, O. — Nunspeet, July 12, 1899; Mr. BEINS.

Perithecia membrana subtilissima praedita, subcutanea, parva, pallida, denique vertice perforata. Sporulae cylindricae vel fusiformes, subcurvatae, stramineae, quadriloculares, ad polos rotundatae, eguttulatae, 14—23 × 4—4$^2/_3$ μ (Pl. IV, fig, 8).

65. HENDERSONIA TYPHICOLA Oud. n. sp. On the stems of *Typha latifolia.* — Nunspeet, May 21, 1899; Mr. BEINS.

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Perithecia primo epidermide velata, denique exposita, tenera, membranacea, parva, subfuliginea, denique vertice perforata. Sporulae oblongae, ad polos rotundatae, rectae vel curvatae, pallide-olivaceae, quadriloculares, $11^2/_3$—$14 \times 4^2/_3$—$5\ \mu$ (Pl. IV, fig. 9).

*HENDERSONIA WEIGELIAE Oud. n. sp. On branches of *Weigelia amabilis*. Nunspeet, March 3, 1898. O. Ned. Kr. Arch. 3, I, 500.

STAGANOSPORA Saccardo.

*STAGONOSPORA DASYCARPI Oud. n. sp. (St. Aceris dasycarpi Ned. Kruidk. Arch. 3, I, 500). — On branches of *Acer dasycarpum*. — Scheveningen, May 1895.

ε. *Dictyosporae.*

CAMAROSPORIUM Schultz.

*CAMAROSPORIUM DASYCARPI Oud. n. sp. — This name should replace that of *Camarosporium Aceris dasycarpi*, used in the Ned. Kr. Arch. 3, I, 501 and in Hedwigia XXXVII (1898) p. 179. On the branches of *Acer dasycarpum*. — Scheveningen, May 1894.

*CAMAROSPORIUM ILICIS Oud. n. sp. N. K. A. 3, I, 502 and Hedw. XXXVII, 1898, p. 179). — On the branches of *Ilex Aquifolium*. — the Hague 1894.

*CAMAROSPORIUM PERICLYMENI. Oud. n. sp. N. K. A. 3, I, 502 and Hedw. XXXVII, 1898, p. 179. — On branches of *Lonicera Periclymenum*. — Scheveningen, Aug. 1894.

66. CAMAROSPORIUM TANACETI Oud. n. sp. — On the stems of *Tanacetum vulgare*. — Nunspeet, Febr. 15, 1899; Mr. BEINS.

Perithecia numerosa, epidermide velata, nunc inordinate sparsa, tunc vero in series lineares digesta, inter peridermatis lacinias ruptas prominentia, semiorbicularia vel anguste-elliptica, glabra, nigra, $^1/_2$ mill. in diam. Sporulae suborbiculares, ellipticae vel late ovatae, vulgo $14 \times 9\ \mu$, quadriloculares, loculo alterutro intermedio septo longitudinali, perpendiculari vel declivi, diviso.

η. *Scolecosporae.*

SEPTORIA Fries (emend.)

67. SEPTORIA CAPSELLAE Oud. n. sp. — On the dry and nearly decayed leaves of *Capsella Bursa pastoris*. — Apeldoorn,

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July 26, 1899; Oud. — Perithecia minima, dense congesta, nigra. Sporulae cylindricae, rectae, curvatae vel flexuosae, hyalinae, ad polos rotundatae, quadriloculares, maturae 50—60 × $2^1/_2$—$3^1/_2$ μ.

68. SEPTORIA CONORUM (Sacc.) Oud.; Phoma Conorum Sacc. Mich II, 615; id. Syll. III, 150. — On the cone-scales of *Abies excelsa*. — Forest of Bloemendaal, Maart 12, 1900; C. J. J. VAN HALL. — Perithecia innato-erumpentia, globoso-depressa, astoma, jure crassiora, carbonacea, nigra, nucleo griseo. Sporulae fusoideae, rectae, 10—14 × 2—$2^1/_3$ μ, primitus 1-guttulatae, postremo septo transverso in partes 2 aequales divisae, basidiis sporis duplo longioribus, post lapsum sporularum uncinatis (Pl. IV, fig. 10).

69. SEPTORIA JAPONICAE Oud. n. sp. — On the leaves of *Evonymus japonica*. — Naaldwijk, 1867; the late Dr. J. E. VAN DER TRAPPEN.

Maculae pallescentes. Perithecia amphigena, inordinate distributa, dense congesta, primo epidermide velata, postea prominentia et epermidis ruptae laciniis dentiformibus erectis circumcincta, nigra, p. m. micantia. Sporulae breve-fusiformes, 15 × 4—5 μ, hyalinae, continuae, rectae, eguttalatae, anguste ad polos rotundatae. — Differt a *Sept. Evonymi japonicae* Pass. (Sacc. Syll. III, 482) sporulis latioribus (15 × 4—5 contra 12—13 × 2.5 μ) et linea alba orbiculari ad verticem peritheciorum absentia (Pl. IV, fig. 11).

70. SEPTORIA OBESISPORA Oud. n. sp. — On the leaves of *Calystegia sepium*. — Nunspeet, Aug. 15, 1898; Mr. BEINS.

Maculae quoad formam et dimensiones admodum variabiles, solitariae vel confluentes, rufescentes. Perithecia epiphylla, minima, inordinate distributa, nigra. Sporulae bacillares, rectae vel curvatae, imo nonnumquam geniculatae, hyalinae, ad polos rotundatae, pluriseptatae, loculamentis omnibus uniguttulatis, 23—28 × 4—5 μ. — Differt a *S. Convolvuli* Desm. sporulis multo crassioribus (23—28 × 4—5 μ contra 35—50 × 1.5 μ); a *S. Calystegiae* West., sporulis brevioribus (23—28 × 4—5 contra 36—45 × 4—5 μ), tandem a *S. flagellari* Ellis et Everhart sporulis brevioribus et crassioribus (23—28 × 4—5 μ contra 35—44 × 1.5 μ). (Pl. IV, fig. 12).

RHABDOSPORA Montagne.

71. RHABDOSPORA ERYNGICOLA Oud. et Sydow n. sp. — Septoria eryngicola Oud. et Sacc. Syll. Addit. ad. vol. I—IV, p. 345, sub.

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no. 298; Sacc. (Syll. X, 367, sub 108). — On the stems of *Eryngium maritimum*. — Scheveningen, Oct. 1892.

Internodia albido-pallescentia peritheciorum numero notabili obducta, quorum maxima $^1/_4$ mill. in diam. habent. Perithecia nigra, primitus epidermide velata, postea vero exposita, vertice perforata. Sporulae curvatae, continuae, eguttulatae, $28—30 \times 1^1/_2 \mu$.

Though *Septoria Eryngii* Pass. (Fghi. Parm. Septoria no. 57 and Sacc. Syll. III, 532), by Professor SACCARDO and myself had formerly been declared identic with *Septoria eryngicola* Oud. and Sacc., it will now appear to me that this view was contrary to the nature of the facts, as *Septoria Eryngii* not only attacks the *leaves* of *Eryngium campestre*, but as moreover its spores get no longer than $20—25 \mu$.

Everything well considered, it seems to me that *Septoria Eryngii* West. (Not. V, 31) with its straight spores of $50 \times 2^1/_2 \mu$ belongs to *Eryngium maritimum*, and that *Septoria eryngicola* Oud. (= S. Eryngii Pass. l. c. = S. eryngicola Oud. et Sacc.), with its straight or curved spores of $25 \times 1—1^1/_2 \mu$, is exclusively found on the leaves of *Er. campestre*. — *Rhabdospora Eryngicola* Oud. et Syd. then represents a third species proper to *Er. maritimum*, whose curved spores of $28-30 \times 2^1/_2 \mu$, keep the middle between those of the two other species mentioned just now.

72. RHABDOSPORA MILLEFOLII Oud. n. sp. — On the stems of *Achillea Millefolium*. — Nunspeet, May 21, 1899; Mr. BEINS.

Perithecia numerosa, densissime congesta, solitaria vel confluentia, in series longitudinales, caulium sulcos implentes, coalescentia, semiglobosa vel a latere compressa et hinc cristiformia, glabra, nigra, primitus epidermide velata, denique exposita et centro perforata, mill. $^1/_3—^1/_2$ in diam. Sporulae bacillares, rectae vel curvulae, ad polos rotundatae, primo 3-, postea 2-guttulatae, continuae, hyalinae, $9^1/_3—11^2/_3 \times 2^1/_3 \mu$, basidiis aequilongis vel longioribus suffultae (Pl. IV, fig. 13).

Differt a *Rh. Achilleae* Bresadola (Roum. Revue Myc. XIII, 1891, p. 30 et tab. CXIV, fig. IX; Sacc. Syll. X, 394) peritheciis multo majoribus et sporulis bis minoribus.

73. RHABDOSPORA TANACETI Oud. n. sp. — On the stems of *Tanacetum vulgare*. — Nunspeet, April 7, 1899; Mr. BEINS.

Perithecia gregaria, punctiformia, epidermide velata, nigra, solidiuscula, $90—120 \mu$ in diam. Sporulae filiformes, hyalinae, rectae,

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curvulae vel p. m. flexuosae, 3-septatae, sub lente multum augente neque guttiferae, neque protoplasmate granuloso farctae, 50—60 × 2 μ.

CYTOSPORINA Saccardo.

*Cytosporina Abietis Oud. n. sp. — On the foremost portion of the under surface of fruit-scales of *Abies excelsa*. — Nunspeet, April 8, 1898; Mr. Beins. Cf. Hedw. XXXVII (1898), p. 317.

74. Cytosporina Syringae Oud. n. sp. — On the branches of *Syringa vulgaris*. — Nunspeet 1898; Mr. Beins.

Stromata corticola, immersa, nigra, oblonga, rima longitudinali sinuosa exarata, intus in loculamenta plura p. m. completa sporulasque foventia divisa. Sporulae filiformes, uncinato-curvatae, continuae, hyalinae, eguttulatae, 32×2 μ, basidiis filiformibus aequilongis fultae.

b. **Nectroideae.**

SPHAERONEMELLA Karsten.

75. Sphaeronemella Wentii Oud. n. sp. (Dedicated to Dr. F. A. F. C. Went, Professor in Botanics at the University of Utrecht). — On the putrefying stems of *Faba vulgaris*. — Utrecht, 1900; Mr. Pulle, candidate of Pharmacy.

Perithecia subglobosa, membranacea, mollia, primo alba, deinde ochracea, cava, 300 μ in diam., sparsa, in telis putrescentibus immersa, rostro concolore subulato circa 900 μ longo coronata. Rostrum e filis tenerrimis, primo per totam longitudinem unitis, postremo versus apicem rostri relaxatis, solutis, retrorsum arcuatis, compositum. Sporulae, basidiis brevissimis e mycelio, conceptaculi fundum obtegente, sursum tendentibus fultae, maturae decidunt et deinde, in guttulam mucilaginis ope conglobatae, ad orificium rostri apparent. Guttula viscosa, in corpora quibusum in contactum venit statim diffluens, diam. habet 250 μ, et colore albo, nec minus nitore suo oculos allicit. Sporulae hyalinae, ellipticae, continuae, longae 7 μ, latae 4 μ.

c. **Leptostromaceae.**

LEPTOTHYRIUM Kunze et Schmidt.

76. Leptothyrium Betuli Oud. n. sp. — On the leaves of *Carpinus Betulus*. — Nunspeet, Nov. 5, 1899; Mr. Beins.

Maculae nullae. Perithecia scutiformia hypogena, numerosa, aequaliter distributa, puncta nigra, convexa, rugulosa, $^1/_{12}$—$^1/_{10}$ mill. in diam. simulantia. Scutula, ex cuticula mutata et atrata formata, itaque

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omnis structurae expertia, cavernulas obtegunt minimas, sporulis minutissimis ($7 \times 1^1/_6\ \mu$), bacillaribus, vulgo curvatis, continuis, eguttulatis, utrimque rotundatis, basidiis aegre distinguendis fultis, repletas.

77. LEPTOTHYRIUM FUNCKIAE Oud. n. sp. — On the leaves of *Funckia ovata*. — Nunspeet, Oct. 11, 1898; Mr. BEINS.

Maculae nullae. Perithecia in facie foliorum inferiore p. m. regulariter distributa, $^1/_6$—$^1/_4$ mill. in diam., nigra, perfecte circumscisso-soluta, ad marginem subtilissime fimbriata, orificio nullo. Sporulae cylindraceae, rectae, ad polos rotundatae, hyalinae, eguttulatae, $2 \times {}^1/_2\ \mu$.

LEPTOSTROMA Fries.

78. LEPTOSTROMA ABROTANI Oud. n. sp. — On the stems and branchlets of *Artemisia Abrotanum*. — Nunspeet, 1899; Mr. BEINS.

Perithecia dimidiata, aequaliter distributa, $^1/_2$—$1^1/_2$ mill. longa, primo epidermide vel peridermate nigrefacto velata, postea exposita, $^1/_3$—$^1/_2$ mill. lata, astoma, saturate-fusca, opaca. Sporulae numerosissimae, hyalinae, continuae, vulgo oblongae vel fusiformes, 7—$10 \times 2^1/_3$—$3\ \mu$, nonnumquam reniformes, $7 \times 3\ \mu$, semper biocellatae, ad polos rotundatae.

79. LEPTOSTROMA LONICERICOLUM Rabh. Bot. Zeit. 1846, p. 46 (nomen tantum); Rab. H. M. I, N°. 865; Sacc. Syll. III, 647 (nomen tantum). On the branches of *Lonicera Caprifolium* var. *coccinea*. — Nunspeet 1899; Mr. BEINS.

Perithecia inordinate sparsa, cuticula tenuissima velata, planoconvexa, atra, nitida, oblonga, centro prominentia, ad polos declivia et acutata, 1 mill. longa, $^1/_2$ mill. lata, tandem poro pertusa. Sporae oblongae vel fusiformes, hyalinae, continuae, biocellatae, $7 \times 2^1/_3\ \mu$, ad polos rotundatae vel acutatae, singulae basidio filiformi tenuissimo, sporulis bis ad quater longioribus suffultae. — Internodia perithecii-gera pallescentia, albida vel straminei coloris.

80. LEPTOSTROMA STELLARIAE Kirchner, Lotos 1856, p. 204; Sacc. Syll. III, 647. — On the leaves of *Stellaria Holostea*, in company with *Septoria Holosteae* Oud. — Nunspeet, April 17, 1899; Mr. BEINS.

Species adhuc indescripta.

Perithecia epiphylla, dimidiata, in maculis pallidioribus foliorum exsiccatorum inordinate-destributa, late-elliptica, convexa, rufo-nigra, opaca, $^1/_2$—$^3/_4 \times {}^1/_3$—$^1/_2\ \mu$, epidermide velata, tandem fissura longitu-

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dinali hiascentia. Sporulae cylindraceo-fusiformes, $9^1/_3$—$11^2/_3 \times 2^1/_3$—$2^1/_2$ μ, ad polos anguste-rotundatae, continuae, hyalinae, biocellatae.

The above description, the first given of this fungus, qualifies us to remove it from the list of the "Species vix notae" (Sacc. Syll. III, 647).

SACIDIUM Nees.

81. SACIDIUM ABIETIS Oud. n. sp. — In sulco longitudinali mediano faciei superioris, et juxta nervum medianum prominentem faciei inferioris acuum *Abietis grandis* cultae, puncta nigra numerosa approximata offenduntur, quae, oculo armato examinata, vesiculas simulant minimas, omnis structurae expertes, 60—100 μ in diam. habentes, colore dilute fuligineo affectas, basin versus in pedicellum brevissimum, quamvis amplum, contractas, sporulis singulis basidio filiformi fultis, repletas. Ipsae sporulae numerosissimae, ellipticae, hyalinae, continuae, guttula mediana ampla, valde micante, praeditae, 9—13 μ longae, 7—9.5 μ latae. — Nunspeet, Sept. 1899; Mr. BEINS. On the leaves of *Abies grandis*.

Sacidium Abietis Oud.

82. SACIDIUM QUERCUS Oud. n. sp. On the leaves of an American species of *Quercus*. — Nunspeet, April 11, 1898; Mr. BEINS.

Perithecia hypogena, caespitosa, orbicularia vel elliptica, 160 ad 180 μ lata, inaequaliter inflata, postremo plana et rugosa, dimidiata, clypeata, atra, astoma, ad faciem internam basidiis numerosissimis, sporuliferis obsessa. Basidia dense congesta, filiformia, 14—$18^2/_3 \times 1^1/_6$ μ, recta, hyalina, continua. Sporulae bacillares, hyalinae, continuae, $6 \times 1^1/_6$ μ.

PIROSTOMA Fries.

83. PIROSTOMA CIRCINANS Fr. S. V. Sc. 395; Fuck Symb. 401; Sacc. Syll. III, 653. On the leaves and leaf-sheaths of *Phragmites communis*. — Nunspeet, 1899; Mr. BEINS.

Badly known species!

When consulting the different authors who have occupied themselves with *Pirostoma circinans*, it is difficult, if not impossible, to imagine that their communications regard the same fungus, though all, for starting point, applied themselves to objects which, although denominated differently, such as *Coniosporium circinans* Fr. S. M. III, 257; West. Herb. Cr. n°. 38; *Sphaeria circinans* Rab. Kr. Fl.

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174; Kickx Crypt. des Flandres I, 349; Lambotte, Fl, Mycol. Belge II, 240; *Pirostoma circinans* Fr. S. V. S. 395; Sacc. Syll. III, 653; Fuck. Symb. 401, — were notwithstanding considered by all of them as no more but synonymes.

Indeed, while some (Fries S. M. III, 257; Rab. Kr. Fl. 174, Lambotte Fl. Mycol. Belge II, 240) make mention of a Sphaeriacee, possessing "globular perithecia perforated at their summit", nay even "asci and paraphyses" (Fr. S. V. S. 395; Kickx l. c.; Lamb. l. c.), others wish the fungus to be allowed but an inferior rank among the Sphaeropsideae, to which asci and paraphyses are wanting (Fuck. l. c.; Sacc. Syll. III, 653). WALLROTH, who endowed our fungus with the name of Sphaeria stigmatella (Flora Crypt. II, 786), ascribes it "very small, slightly-globose perithecia which are closely pressed against the plant", while FUCKEL, adopting the nomenclature of FRIES, declares notwithstanding: „Ich kann mir ueber den Bau dieses Pilzes noch kein klares Bild entwerfen." The characteristics of the genus he passes by, but admits that the species has globular, brown stylospores of 12 μ diameter, concealed under a lengthwise stretched peltate perithecium.

The supposition that the different authors have possibly devoted their investigations to two different species, may be represented as acceptable, still it ought to be rejected, when considering that as well FRIES, who introduced the name of *Coniosporium*, as RABENHORST KICKX and LAMBOTTE, who served themselves of the expression *Sphaeria* to elucidate their divergent opinions, refer all to N°. 330 of the "Plantes Cryptogames du Nord de la France 1e Ed. (A°. 1828)", which — as is proved by the words added to the name of „*Pirostoma circinans*": „FRIES, in litteris", sent to the renowned mycologue to be verified — shows neither perithecia, nor asci, nor paraphyses, and which, moreover, consists of nothing else but very small, flat, perfectly sterile shields, not unlike those which are characteristic of the genus *Leptothyrium*.

The specimens of *Pirostoma circinans*, published by FUCKEL in his Fungi Rhenani under N°. 791, not without the synonymes *Coniosporium circinans* and *Sphaeria circinans* being added to the chief name, differ in no single respect from those of DESMAZIÈRES, while these, in their turn, cannot be distinguished from those of the "Herbier des Cryptogames Belges" of WESTENDORP (N°. 38).

The specimens collected in Holland of *Pirostoma circinans*, for the greater part in excellent condition, deviate in no single respect from those of:

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1. DESMAZIÈRE's Plantes Cryptogames du Nord de la France, 1e Ed., No. 330 (Coniosporium);
2. RABENHORST's Herbarium mycologicum, 2e Ed. No. 59 (Coniosporium);
3. RABENHORST's Fungi Europaei, Nos. 1031 en 2700 (Pirostoma);
4. WESTENDORP's Herbier Cryptogamique Belge, No. 38 (Sphaeria);
5. FUCKEL's Fungi Rhenani, No. 791 (Pirostoma);
6. ROUMEGUÈRE's Fungi gallici, No. 1082 (Pirostoma);

which means, that the microscopic investigation of all these collections may be considered as to be described in the following lines.

Pirostoma circinans, a fungus, hitherto found nowhere but on the stems and leaf-sheaths of *Phragmites communis*, appears at macroscopic examination in the shape of stripes, dots, or rings (whence the name of *circinans*), of more or less length, circumference, or diameter, which are first hidden under the cuticula, but later throw off that membrane and then show a brown tint, which in older objects inclines to black and, when struck by sunlight, displays more or less gloss.

When examined with the microscope, the black portions show a finely granulous surface, which has probably given cause to the mentioning of an "accumulation of very minute, densely crowded perithecia", which expression is still met with in some authors. We must directly add, however, that this conception reposes on an error, and that in *Pirostoma* there are found no perithecia at all, and accordingly neither asci and paraphyses.

A single granule, subjected to microscopic examination, presents itself as a low, dome-shaped body, or, in other words, as a plane-convex (hollow) lens, of which the convex side is turned toward the spectator, while the flat one reposes on the object which bears the fungus. The convex side is composed of extremely minute blown-up cells, which, seen in front, are $2^1/_3$ to $4^2/_3\ \mu$ wide, and angular, and have this peculiarity, that the black colour proper to them and on which depends the dark appearance of the stripes, dots, and rings, proves to be limited to that outerside, whilst the side-walls and the inner-wall are wholly devoid of it. Add to this that the coloured side in the middle, or close by, shows an extremely small hole at the bottom of a superficial impression, and that this hole has the appearance of a brilliant point because it allows the eye

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to penetrate into the colourless back-wall of the cell and into the colourless tissue behind it, — then it can hardly be denied, that this concurrence of facts can give rise to the conviction that no better name than that of *Pirostoma* (derived from the Greek words *πείρω* to pierce, and *στόμα* mouth or opening) could have been chosen to indicate the properties, which we have above drawn attention to. Still there is no doubt that FRIES, whose diagnoses sprung from researches with no other instrument but the magnifying-glass, cannot have been acquainted with the finer structure sketched by us just now, whence it follows that in giving the name of *Pirostoma* to objects quite like to those which we examined ourselves, he will have been led: not by examining the cells of the small granulous corpuscula, but by the black spots themselves, at which we, however, never observed anything like an opening. For the rest we repeat that the presence of "sporae ascis linearibus paraphysophoris receptae" has neither been found true by ourselves, nor by FUCKEL, nor by SACCARDO, so that the fungus, endowed by FRIES with the name of Pirostoma circinans, has remained a riddle to us. The information of KICKX and LAMBOTTE, of whom the latter did nothing but simply copying the formula produced by the former, and that imperfectly, too, cannot relieve our embarrassment, as they refer their readers to the dried objects of WESTENDORP, at which nothing can be discovered of what they describe; on the contrary, everything corresponds with what we have found in our own specimens.

After mature consideration, *Pirostoma circinans* appears to us a preliminary, sterile condition of a higher form, and allied to the genus *Leptothyrium*. SACCARDO gave the fungus a place among his „Leptostromaceae phaeosporae", no doubt because FUCKEL had attributed to it "globular, brownish stylospores", still we can attach no value to this view as it is completely contrary to the experience acquired in the investigation of FUCKEL's exsiccata.

All those who attribute to *Pirostoma circinans* an ostiolum, asci, spores, and paraphyses, seem to have examined some or other Pyrenomycete, accidentally got among the shields of Pirostoma or, without previous research, to have copied the mycologue of Upsala, or one another.

d. **Excipulaceae.**

DISCELLA Berkeley et Broome.

84. DISCELLA BERBERIDIS Oud. n. sp. (Discella Grossulariae Oud. Ned. Kruidk. Arch. 2, V, 506). After it had appeared to me that

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the branchlet on which I had found the above mentioned *Discella* had not belonged to *Ribes Grossularia*, but to *Berberis vulgaris*, the first chosen name had of course to be changed. So I here redress the error committed while calling to mind that the diagnosis of the fungus ran as follows:

Maculae circulares nigrae numerosae, $^1/_{10}$—$^1/_5$ mill. in diam., micantes, primo neutiquam, postremo parum prominentes, e cellulis peridermatis, pseudoparenchymate nigrescente repletis, formatae, foveas minimas, in parenchymate corticali absconditas, operculi ad instar occludunt. Foveae, sporularum glebula coloris mellei repletae, peritheciorum locum tenent operculoque scutiformi perforato vel delapso late patentes, contenta amittunt. Sporulae bacillares, rectae vel subcurvatae, ad polos rotundatae, biloculares, separatim visae fere hyalinae, congestae vero manifeste mellae, $7—10 \times 2—3\ \mu$.

(To be continued).

Mathematics. — "*On the* MACMAHON *generalization of the* NEWTON-GIRARD *formulae*". By Prof. L. GEGENBAUER of Vienna (Communicated by Prof. JAN DE VRIES).

In his treatise contained in the 15th volume of the "Proceedings of the London Mathematical Society" "On Symmetric Functions and in particular on certain Inverse Operators in connection therewith" MACMAHON has deduced with the aid of differential operators the relations

$$S^m_{m+r} - f_1 S^m_{m+r-1} + f_2 S^m_{m+r-2} - \ldots + (-1)^r f_r S^m_m = (-1)^r \frac{(r+m)!}{r!\, m!} f_{m+r}$$

where S^i_k denote those symmetric functions of dimension k in the n quantities $x_1, x_2, \ldots, x_n$ in which every term contains i of these quantities, so that in particular S^i_i is their elementary symmetric function f_i and S^1_k the sum of their k^{th} powers.

These relations forming an interesting generalisation of the NEWTON-GIRARD formulae, were proved anew somewhat later by LACHLAN in his paper „On certain Operators in connection with Symmetric Functions" published in the 18th vol. of the same „Proceedings". Other deductions of these formulae have as yet not caught my eye; neither

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are any others mentioned in the article referring to it of the „Encyklopädie der mathematischen Wissenschaften" (Teil I, Bd. I, p. 449—479). However, it being not impossible, that one might wish to read about these relations in the elementary algebraic lessons, where either no use can or will be made of the differential operators, I will communicate in the following lines a proof founded upon another completely elementary basis, which has moreover another advantage of being entirely analogous to the other one, which is usually given for the special case $m=1$ (NEWTON-GIRARD formulae).

1. The NEWTON-GIRARD formulae are generally deduced by comparison of the coefficients of the different powers of x in the two members of the equation

$$f'(x) = \sum_{\lambda=1}^{\lambda=n} \frac{f(x)}{x-x_\lambda} = \sum_{\lambda=1}^{\lambda=n} f_1(x\,;\,x_\lambda) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $f(x)$ is a polynomium of degree n and $x_1, x_2, \ldots, x_n$ are its roots. For the sake of simplicity we shall take the coefficient of x^n equal to 1. This proof is based on the double representation of the *first* derivative of a polynomium. In quite an analogous way the general relations can be found by means of a double representation of the m^{th} derivative of such a polynomium.

By differentiating the equation according to x_1 we obtain

$$f''(x) = \sum_{\lambda=1}^{\lambda=n} f_1(x\,;\,x_\lambda)$$

or with the aid of (1)

$$f''(x) = \sum_{\lambda,\mu=1}^{\lambda,\mu=n} \frac{f(x)}{(x-x_\lambda)(x-x_\mu)} = \sum_{\lambda,\mu=1}^{\lambda,\mu=n} f_2(x\,;\,x_\lambda, x_\mu) \left(\lambda \gtrless \mu\right).$$

By successive differentiation we arrive at last at

$$f^{(m)}(x) = \sum_{\lambda_1,\lambda_2,\ldots\lambda_m} \frac{f(x)}{(x-x_{\lambda_1})(x-x_{\lambda_2})\ldots(x-x_{\lambda_m})} (\lambda_1, \lambda_2, \ldots, \lambda_m = 1,2,\ldots,n;\ \lambda_i \gtrless \lambda_k, i \gtrless k).$$

Now we find that

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$$\frac{f(x)}{(x-x_{\lambda_1})(x-x_{\lambda_2})\ldots(x-x_{\lambda_m})} = x^{n-m} + (x_{\lambda_1} + x_{\lambda_2} + \ldots + x_{\lambda_m} - f_1)\,x^{n-m-1} +$$

$$+ \Big[x_{\lambda_1}^2 + x_{\lambda_2}^2 + \ldots + x_{\lambda_m}^2 + x_{\lambda_1}x_{\lambda_2} + x_{\lambda_1}x_{\lambda_3} + \ldots + x_{\lambda_{m-1}}x_{\lambda_m} -$$

$$- f_1(x_{\lambda_1} + x_{\lambda_2} + \ldots + x_{\lambda_m}) + f_2\Big]\,x^{n-m-2} +$$

$$+ \Big[x_{\lambda_1}^3 + x_{\lambda_2}^3 + \ldots + x_{\lambda_m}^3 + x_{\lambda_1}^2 x_{\lambda_2} + x_{\lambda_2}^2 x_{\lambda_1} + x_{\lambda_1}^2 x_{\lambda_3} + x_{\lambda_3}^2 x_{\lambda_1} + \ldots +$$

$$+ x_{\lambda_{m-1}}^2 x_{\lambda_m} + x_{\lambda_m}^2 x_{\lambda_{m-1}} + x_{\lambda_1}x_{\lambda_2}x_{\lambda_3} + x_{\lambda_1}x_{\lambda_2}x_{\lambda_4} + \ldots + x_{\lambda_{m-2}}x_{\lambda_{m-1}}x_{\lambda_m} -$$

$$- f_1(x_{\lambda_1}^2 + x_{\lambda_2}^2 + \ldots + x_{\lambda_m}^2 + x_{\lambda_1}x_{\lambda_2} + x_{\lambda_1}x_{\lambda_3} + \ldots + x_{\lambda_{m-1}}x_{\lambda_m}) +$$

$$+ f_2(x_{\lambda_1} + x_{\lambda_2} + \ldots + x_{\lambda_m}) - f_3\Big]\,x^{n-m-3} + \ldots .$$

. . . . . .

Effecting in this equation the indicated summation according to the quantities $\lambda_1, \lambda_2, \ldots, \lambda_m$, we find that of every single term on the right side $\frac{n!}{(n-m)!}$ terms are formed; amongst the group of those, which form the coefficient of $x^{n-m-\rho-\sigma}$, each term necessary for the representation of the symmetric function $S^{\rho}_{\rho+\sigma}$ presents itself $\frac{(n-\rho)!\,m!}{(n-m)!\,(m-\rho)!}$ times and so we obtain the relation

$$f^{(m)}(x) = \frac{n!}{(n-m)!}\,x^{n-m} + \sum_{\sigma=1}^{\sigma=n-m} x^{n-m-\sigma}$$

$$\Big[\sum_{k=0}^{k=m} \frac{(n-k)!\,m!}{(n-m)!\,(m-k)!}\Big(S^k_\sigma - f_1 S^k_{\sigma-1} + f_2 S^k_{\sigma-2} - \ldots + (-1)^{\sigma-k} f_{\sigma-k} S^k_k\Big)\Big]$$

when we substitute

$$S^0_0 = 1, \quad S^k_{\sigma_1} = 0 \quad \text{for} \quad k > \sigma_1 .$$

This leads to the relation

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$$(-1)^{\sigma}\frac{(n-\sigma)!}{(n-m-\sigma)!}f_{\sigma}=\sum_{k=0}^{k=m}\frac{(n-k)!\,m!}{(n-m)!\,(m-k)!}\,(S_{\sigma}^{k}-f_1 S_{\sigma-1}^{k}+$$

$$+f_2 S_{\sigma-2}^{k}-\ldots+(-1)^{\sigma-k}f_{\sigma-k}S_{k}^{k}),$$

which can be written as follows

$$S_{m+r}^{m}-f_1 S_{m+r-1}^{m}+f_2 S_{m+r-2}^{m}-\ldots+(-1)^{r}f_r S_{m}^{m}=$$

$$=\frac{(-1)^{m+r}}{m!}\left\{\frac{(n-m-r)!}{(n-2\,m-r)!}f_{m+r}-\sum_{k=0}^{k=m-1}\frac{(n-k)!\,m!}{(n-m)!\,(m-k)!}\right.$$

$$\left.\left(S_{m+r}^{k}-f_1 S_{m+r-1}^{k}+f_2 S_{m+r-2}^{k}-\ldots+(-1)^{m-k}\;f_{m+r-k}S_{k}^{k}\right)\right\}$$

by making $\sigma=m+r$ and by separating the term for $k=m$ on the right side from the sum.

2. Now, if the MacMahon relation exists for all the values of the superior index from 1 to $m-1$ inclusive, this equation transforms itself into

$$S_{m+r}^{m}-f_1 S_{m+r-1}^{m}+f_2 S_{m+r-2}^{m}-\ldots+(-1)^{r}f_r S_{m}^{m}=$$

$$=\frac{(-1)^{m+r}}{m!}\left\{\frac{(n-m-r)!}{(n-2\,m-r)!}-\sum_{k=0}^{k=m-1}(-1)^{k}\frac{(n-k)!\,m!\,(m+r)!}{(n-m)!\,(m-k)!\,(m+r-k)!\,k!}\right\}f_{m+r},$$

which by introduction of the symbol [1])

$$\varphi(m,\lambda,n)=1-\frac{m\,\lambda}{1!\,n}+\frac{m\,(m-1)\,\lambda\,(\lambda-1)}{2!\,n\,(n-1)}-\ldots+(-1)^{m-1}\frac{(n-m)!\,\lambda!}{n!\,(\lambda-m)!}$$

takes the form of

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[1]) In relation to the facts supposed to be known before the demonstration is entered upon with a view to the previously mentioned aim, we remark that the circumstance of $\varphi(m,\lambda,n)$ being finite hypergeometric series with unity as fourth argument at infinity is not made use of.

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$$S^m_{m+r} - f_1 S^m_{m+r-1} + f_2 S^m_{m+r-2} - \ldots + (-1)^r f_r S^m_m =$$

$$= \frac{(-1)^{m+r}}{m!} \left\{ \frac{(n-m-r)!}{(n-2m-r!)} + (-1)^m \frac{(m+r)!}{r!} - \frac{n!}{(n-m)!} \varphi(m, m+r, n) \right\} f_{m+r}(2)$$

3. We find at once for the function $\varphi(m, \lambda, n)$ the equation

$$\varphi(m+1, \lambda, n) = \varphi(m, \lambda, n) - \frac{\lambda}{n} \varphi(m, \lambda-1, n-1),$$

by which it is entirely determinated for all the values of $n > 1$, if moreover the equation

$$\varphi(0, \alpha, \beta) = 1, \qquad (\alpha > 1, \beta \geqq 1)$$

is added.

The quantity

$$\frac{(n-m)!\ (n-\lambda)!}{n!\,(n-m-\lambda)!}$$

satisfying the same functional equation and having likewise for $m = 0$ the value 1, we find

$$\varphi(m, \lambda, n) = \frac{(n-m)!\,(n-\lambda)!}{(n-m-\lambda)!\,n!},$$

which equation holds good, as is easely shown, as long as $n \geqq m$, when for $n < m + \lambda$ the right side is replaced by nought. Particular attention is drawn to the fact, that n, m and λ are supposed to be integers.

4. The equation (2) therefore transforms itself into the following

$$S^m_{m+r} - f_1 S^m_{m+r-1} + f_2 S^m_{m+r-2} - \ldots + (-1)^r f_r S^m_m = (-1)^r \frac{(m+r)!}{m!\ r!} f_{m+r}$$

which teaches us, that the MacMahon relations are true for a definite m for any integer value of r and for $n \geqq m + r$, if they have already been proved for all the minor values of m. This being the case according to the Newton-Girard formulae for $m = 1$ they exist in general.

It would be difficult to give a demonstration of these relations more simple in conception.

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Bacteriology. — "*On different forms of hereditary variation of microbes*". By Prof. M. W. BEIJERINCK.

The interesting lecture of Prof. HUGO DE VRIES in the last meeting of the Academy on the origin of new forms in higher plants, induces me to draw attention to some observations regarding the same subject in microbes.

Though the culture of microbes, compared to that of higher plants and animals is subject to many difficulties, it cannot be denied that, these once mastered, microbes are an extremely useful material for the investigation of the laws of heredity and variability. The starting from the single individual, which of course is required here, is commonly almost as simple as for the higher organisms, and it is want of practice only which makes it appear so troublesome. The generations succeed each other quickly; hundreds, nay thousands of individuals can be very easily surveyed in their posterity; far remote classes of the natural system are represented by microbes; in many the variability is great [1]). Even the difficulty of determining the species and varieties, which is frequently only possible by means of biochemical investigation, can become an advantage, for the very reason that biochemical methods of distinction are very accurate, can be extended in various directions and compared by measurement. Thus the species and varieties of lactic-acid ferments are distinguished by titration, alcohol ferments by means of the saccharometer, while different carbohydrates can be selected as the base of lactic-acid and alcohol fermentation. To all this is added the circumstance that it is easy to perform with microbes experiments of competion, which is difficult or impossible with higher plants and animals, and it is well-known how delicate the distinctions are which are thereby revealed.

In comparing the results obtained with microbes to the rules found in higher organisms, account should be kept, first, with the want of sexuality, by which the variation of microbes becomes comparable to the bud-variation of the higher plants, and, second, with the uni-cellularity of the microbes. As to the first point the experiences with the bud-variants of higher plants seem to prove that an essential difference between bud-variation and seed-variation does not exist. As to the uni-cellularity of the microbes, it is my opinion that by it the phenomena of variation are rendered clearer but are not changed, when

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[1]) Compare RODET, De la variabilité dans les microbes, Paris 1894. Bibliography wants in this book und not all data are trustworthy.

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compared to the multi-cellular organisms. According to the point of view, the individual microbe can be compared to the whole individual of the higher organism, or to a single tissue-cell of it, — both comparisons are correct [1]).

1. *Degeneration.*

In bacteriological laboratories it is well-know that by prolonged culture many microbes undergo slow, but great changes, even in so much, that certain long continued cultures do not agree any more with the descriptions given of them by the discoverers, short after their first isolation from nature. In some cases the way in which the change takes place can be rather minutely traced; three forms of variability are therein more salient: degeneration, transformation and common variation.

A species is isolated from nature and it is found that at the culture during the first series of inoculations, in which hundreds or thousands of cell-generations succeed each other, it develops well, so that in the beginning the impression is obtained of a thorough knowledge of the nutrition and other conditions of life. But by and by it becomes more difficult to make the new inoculations thrive and at last the culture-material grows troublesome and uninteresting and would be quite unrecognisable if not the various phases of the degeneration-process had been exactly observed. Prolonged cultivation above the optimum temperature of the growth, and a too strong concentration of the nutriment are in some cases the cause of degeneration. In some microaërophilae, for instance the bactery of the "lange-wei" *(Streptococcus hollandiae)* [1]), the irrational regulation of the oxygen tension causes a rapid, in few days complete vanishing of the slimeformation, while after a much longer time, by the same cause, the vegetative power of the bactery completely disappears. In other cases, for instance with a phosphorescent bactery, very common in the sea *(Photobacter degenerans* FISCHER*)*, the degeneration is accomplished without known cause, and in a very short time, so that, within a few weeks the cultures may cease to exist. The degeneration goes not by leaps but continuously and affects all the

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[1]) An interesting view herewith connected is found in WHITMAN, The inadequacy of the cell-theory of development. Biological Lectures at the Wood's Holl Laboratory, 1893, pag. 105, Boston 1894.

[2]) Used in Holland for cheese-making.

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individuals in culture equally, so that it cannot be checked by colony-selection.

2. *Transformation.*

At the transformation all the individuals brought in culture lose a characteristic, while either another comes in its place, or a new characteristic arises, or, lastly, the characteristic disappears without a distinct substitute. Thus the cultures of *Photobacter luminosum* grow dark in the course of some months by a slow process of transformation, whereby they change into a more rapidly growing form, which acts more strongly on the nutriment than the normal form. Here, thus increase of vegetative power has supplied the decrease of phosphorescence.

It is remarkable that the transformation in this phosphorescent bactery sometimes suddenly ceases and is replaced by a process of variation where, beside a completely dark form (the variant), the phosphorescent form with the full primitive phosphorescent power again springs up. This is not the same as common atavism, where the stock which throws off the atavist does not change further, but it is probably comparable to the splitting of a bastard into the two components. Very slow cell-partition, caused for instance by culture at a low temperature, furthers this phenomenon. On the other hand, the cause of the transformation may be a too rapid process of cell-partition in which the photoplasm, which seems to grow more slowly than the rest of the protoplasm, remains behind in its development.

In another phosphorescent bactery of the sea, common on our coast, *Ph. hollandiae*, I hitherto only saw transformation, so that this species quickly disappears from the cultures as a phosphorescent bactery.

In a pigment bactery (*Bacillus viridis*) I saw, apparently without any other change, the at first very strong power of liquefying gelatin, by and by get lost in all the individuals.

On the other hand, I have seen in some vibrions, in a corresponding way, from non-gelatin-liquefying individuals come forth liquefying ones.

The new forms, thus called into life give, at superficial examination, quite the impression of new constant species. They cannot, however, be valued as such as they differ only by one or very few characteristics from the mother forms. This is the cause why they must be classified as variants, quite like those of the following case.

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3. *Common variation.*

The third and most frequent form of variability is *common variation*. Here the normal form continues unchanged, but now and then throws off individuals, the variants, which, from the beginning, are likewise constant and remain so, but which every now and then again throw off other variants, among which the normal form may occur as an atavist. These variants probably correspond with many well-known so-called varieties or races of culture plants and domestic animals, and likewise, I should think, with the interesting new forms obtained by Prof DE VRIES from *Oenothera lamarckiana* [1]). They remind us in some respects also of the Pleomorphy in the Fungi, which especially in the Ustilaginae, can easily be observed in the laboratories and about which, in particular BREFELD, has made many researches [2]).

The names variant and sub-variant I have chosen, because in the here discussed products of hereditary variation, which differ apparently very much, but in fact only little from the normal form, I think to see the lowest degrees of the natural system following above the individual, and to them are given those names according to the rules of botanic nomenclature [3]).

Regarding the divisions above the species, DE CANDOLLE does not think it necessary to give definitions, in which I quite agree with him. But singularly enough he does try to do it for the ranks beneath the species, where he takes the greater or lesser constancy at sowing as a criterion for the differences. This is not logical, here too, definitions are unnecessary.

Probably various causes give rise to the production of variants. Lengthened growth at insufficient nutrition, and the prolonged action of the own secretion products of the microbes may, with some probability, be considered as such causes.

The variant seems seldom, perhaps never, by one single cell-partition to result from the mother-form, but only after some intermediary partitions, rapidly accomplished. With these latter partitions correspond the sub-variants, with a disposition for atavism or further variation, and only keepable by colony-selection.

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[1]) These Proceedings. Meeting of 29 Sept. 1900 pag. 246. Comptes rendus. T. 131 pag. 124 en 561, 1900.

[2]) Botanische Untersuchungen über Hefenpilze. Heft 5, 1883.

[3]) A. DE CANDOLLE, Lois de la nomenclature botanique, 2e Ed. pag. 15, 1867, and Nouvelles remarques, pag. 48 and 63, 1883.

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I will now describe some instances of common variation; first a few cases of the originating of hereditary-constant variants, which seem unable to return to the stock, then the more complicated case of constant and variable variants, among which some with a great disposition for atavism, which case I have nearer investigated in the West-Indian phosphorescent bactery and its relatives.

I might augment these instances with many more, for most of the microbes with which I occupied myself for a length of time, produced in my cultures more or less hereditary-constant variants. Extremely variable are the mycelia of the Fungi, for which I refer to the complicated relations of the aethyl-acetate-yeast, which I described and demonstrated in 1895 [1]), and where transformation and common variation both occur.

4. *Variation in Schizosaccharomyces octosporus* [2]).

This curious maltose-yeast I detected in 1893 on dried orient-fruits as currants, dates, raisins, and figs. I found a good method to separate this species from the other microbes, by which it is possible as often as desired to bring it from nature into culture. It proved to be a generally spread organism, which is found in Greece, Turkey, Italy, Asia Minor and Java in one and the same variety. After many isolations I found in 1897 [3]) a new variety on dates from N.-Africa. The culture is effected in the like way as of beer-yeast on wort-gelatin. Maltose, like glucose and levulose, undergoes a vigorous alcoholic fermentation, cane-sugar not at all.

As well the usual form as the new variety produce 8-spored spo-angia, the spores of which colour intensely blue with iodium. During the growing a small quantity of diastase is secreted. The vegetative condition which precedes the spore-formation, as also the vegetative variant, which produces no more spores, of which more below, multiply by partition (not as in other yeasts by budding) and colour yellow by iodium; glycogene wants completely in it. Accordingly it is possible, by treating a culture with iodium, from thousands of colonies, instantly to recognise those containing spores, and from the intensity of the blue-colouring with some certainty to make out

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[1]) Handelingen van het 5e Natuur- en Geneesk. Congres te Amsterdam pag. 301, 1895.

[2]) Centralblatt für Bacteriologie Bd. 16 pag. 49, 1894 and Ibid. Abth. 2. Bd. 3 pag. 449, 1897. In 1897 I put the variant on a level with a "vegetative race", but as I now think, in doing so I rated its systematic value too high.

[3]) Together with a new quite different species of *Schizosaccharomyces*.

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the number of spores present. The variety of dates differs from the main form by the sporangia of the latter being ellipsoidal and thickest in the middle, while in the variety, on the other hand, they are just in the middle constringed, and moreover by several other little salient characteristics, which only become discernible by practice.

Both, main form as well as variety produce, as the cultures grow older, a variant so much deviating from the normal forms, that, if these variants were met with in nature, they would certainly be proclaimed a new species if no new genus. The cells are globular, and not as in the normal form elongated, but the multiplication is here also exclusively effected by partition. Spores are not at all formed.

This variant springs, so far as I have been able to find out till now, at once form the normal form, which for the rest propagates unchanged, and can constantly anew throw off the variant. The first variants are found in cultures which have continued growing a few weeks without re-inoculating, and they go on some time multiplying on the nearly exhausted culture medium, after the normal form does no more do so. This points to a gain of vegetative power, at least in the conditions that prevail in the old culture-medium, but in new nutriment I could observe nothing of this difference.

The variant after repeated re-inoculation, at present already during more than three years and consequently after thousands of cell-generations, has remained perfectly constant; never could even a single sporangium be found, which, with the help of the iodium reaction, can be seen at a glance in the microscopic preparation. Whether in the variant the faculty of forming spores continues latent is possible, even probable, but not proved.

In the variety, isolated from dates, also occur sub-variants, that is intermediary forms between normal form and variant, while in that of currants I have found no sub-variants. The sub-variants still produce some sporangia, mostly 8-spored. Without much trouble I could isolate from a thousand colonies three sub-variants, belonging to two types; both types proved at re-inoculation to be constant, but growing older they throw off, in the habitual way, the asporgene variant, so that, in order to be preserved, they must be propagated from the spores. This can be done by pasteurising the sowing material at 55° C., by which the vegetative cells die and the spores alone survive.

In continuing this manipulation I have obtained new sub-variants. One of these produces 4- or 8-spored globular sporangia and is at

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first sight a new species. Cells and sporangia remind of the vegetative variant which should have regained the power of producing spores. But all the characteristics are limited between those of the normal form and the asporogene variant. So that, although this form too is hereditary-constant, I cannot see a new variety in it, but only a new variant.

It is noteworthy in this case, that the variants of the same generation, that is those which result from the same sowing, always differ by distinct breaks in the tint of the iodium reaction, and form no flowing series between main form and main variant. But I think this to be the consequence of the limited number of colonies which can be overseen at each experiment, and amount to no more than one or two thousand, and that it will be possible to fill up the gaps with sub-variants from other cultures, which perhaps grow rarer as the leaps are smaller. The question why sub-variants are so much rarer than main variants, I cannot as yet fully answer, but the existence of sub-variants proves that the great and sudden leaps, observed in the variability everywhere in the vegetable and animal kingdoms, are no necessary attribute of variability. Furthermore these sub-variants prove that even slight deviations may be in high degree hereditary-constant [1]).

5. *Variation in Bacillus prodigiosus.*

This well-known red pigment-bactery is cultured by me in three distinct natural varieties. One of them does not liquefy the the culture-gelatin [2]), of the two others which do, one [3]) has the power of causing various carbon-hydrates to ferment under production of hydrogen, the other not [4]). All three produce, in older cultures, a variant which is completely colourless, but in all other respects possesses the properties of the normal form whence it has taken birth, so that there are non-liquefying and fermenting, and liquefying non-fermenting colourless variants. All these variants have remained hereditary-constant in my experiments and produce no

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[1]) For the more complicated phenomena of variation in some species of *Saccharomyces*, I refer to my paper "Sur la régénération des spores chez les levûres etc., Archives Néerlandaises, Sér 2, T. 2 pag. 269, 1899.

[2]) Isolated from potatoes grown hollow in the soil and given me by Prof. RITZEMA BOS.

[3]) Isolated from tubercles of red clover.

[4]) Isolated from bones kept at the open air on the bone-hill of the gelatin- and glue-factory at Delft.

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atavists like to the mother form, i. e. red-coloured colonies. There is no doubt but, if these variants were met with in nature, not accompanied by the normal form from which they arise, they would be taken for as many new species. Still it would be an error to admit them as species into the system, as a more minute investigation shows that, except in the power of forming pigment, they correspond in all other respects with the normal forms, and one single point of difference determines only a variant.

I doubt by no means that *B. prodigiosus* can also vary in other directions; this follows already from the fact that I could find three very different natural varieties, which all produce red pigment [1]). But I have not taken pains to trace other variations.

Sub-variants between the normal forms and the said colourless variants are, or at least seem rarer than the main variants. They are rose-coloured and at colony-selection almost as constant as the normal form. They also produce like the latter the constant colourless main-variant, and moreover show a propensity for atavism. In each natural variety I have found only one or two rose-coloured sub-variants.

6. *Variation in Photobacter indicum.*

This phosphorescent bactery was isolated by Prof. FISCHER of Kiel, from seawater in the vicinity of the isle of Santa Cruz, one of the Antillies, on January 10, 1886. I received material of it in May 1887 and have without interruption cultured it till now. Already in 1887 I perceived, that with the growing older of the cultures, two main variants arise and even in so great a number that the normal form can be supplanted by them for the greater part, though not quite. One of these is either completely or almost completely dark, the other grows much more slowly than the normal form and is almost motionless, while the normal form is extremely motile. I will call these variants *Ph. indicum* vnt. *obscurum* and *Ph. indicum* vnt. *parvum*. Later I found some more variants which are less common. There are besides sub-variants of which I have examined those standing between the normal form and *obscurum*; they produce now and then atavists, and vary also towards *obscurum*, but can be kept constant by colony-selection.

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[1]) The red pigment of *B. prodigiosus* is a product of excretion found between the living and partly accumulated in dead bacteria. It is in my opinion the product of specific chromoplasm, which forms a small part of the protoplasm in general.

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Notwithstanding this great variability it has been possible, likewise by means of colony-selection, during the more than 13 years continued laboratory culture, to keep up the stock unchanged, which is remarkable, when thinking of the place where it was first found.

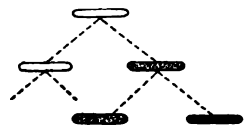
The variants and sub-variants always spring from the stock in the same way. They may be reduced to two types: variable and unvariable. All phosphorescent variants are more or less variable.

The variant *parvum* shows an extreme disposition for atavism, so that already after its first re-inoculation on a new culture-medium, various normal forms spring from it.

The *obscurum*-variants are more constant. They are either perfectly constant, so that, as it seems, phosphorescent forms never again arise from them, or imperfectly, so that after going through a few cell-partitions, answering to as many sub-variants, the normal form returns with the full phosphorescent power. Dark variants, in this way producing luminous cultures, prove that progressive variability [1]) also occurs in the laboratory cultures

The variant is not the product of a single heterogene cell-partition, but of the passing through some preparatory cell-partitions, answering to as many sub-variants. I was able without difficulty to distinguish two of these leaps or sub-variants, but it is possible that there are more, too slightly differing for my observation. It is also probable that by the conditions of culture, these preparatory cell-partitions, and with them the sub-variants, existing between the normal form and the main variant, will grow more or less numerous.

Fig. 1.



Probable course of development of the dark variant by direct heterogene cell-partition or evolution. The first partition produces from the single luminous bacillus one of the same, and another of lessened luminosity. The second partition produces from the latter again one of the same luminosity, and another quite-dark.

The *obscurum*-variant is probably produced in accordance with the scheme of Fig. 1.

For the sake of simplicity here is only figured one intermediary stadium (sub-variant) by the dotted rod; the dark main variant is drawn black, the normal form white. This scheme answers to what may be called the development of the cell-variant by heterogene cell-partition or evolution.

Less probable is the development of the variant by transformation or epigenesis represented in Fig. 2.

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[1]) Distinction can be made between: — retrograding or analytic variability, in which a characteristic disappears entirely or partly, — replacing variability, in which a characteristic is wholly or partly supplanted by another, — and progressive or synthetic variability, in which a new characteristic is added to those already existing.

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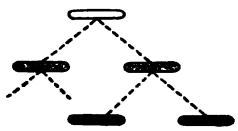
Fig. 2.

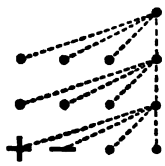


Less probable course of development of variant by indirect heterogene cell-partition or epigenesis.

The preparatory cell-partitions at the atavism of the luminous normal form from the dark or feebly luminous sub-variants still liable to retrogression, probably answer likewise to the schema of Fig. 1.

If the normal form is indicated by •, the *obscurum*-variant by —, and the *parvum*-variant by +, unreckoned the sub-variants, the pedigree of the normal form of *Ph. indicum* can be represented by Fig. 3, which means, that at the two first re-inoculations only the normal form is produced, and that at the third likewise *obscurum*- and *parvum*-variants have orginated, but from cells which were subjected to particular conditions. The numbers 2 and 3 for the generations are chosen arbitrarily, for the number of generations, after which the variation occurs, can be regulated at will, for by early re-inoculating the young cultures on fish-broth-agar (not on fish-broth-gelatin) the variation can be kept back for a long time [1]).

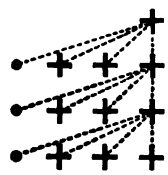
Fig. 3.



Pedigree of *Ph. indicum*, normal form.

For the variant *parvum* the pedigree becomes somewhat different from that of the normal form, there being much atavism (Fig. 4).

Fig. 4.

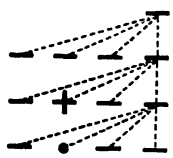


Pedigree of *parvum*.

The pedigree of *obscurum* can, as to the constant form, be represented by a single mark.

The variable, *obscurum*, again produces atavists, but less than *parvum*, and besides *parvum*-variants (Fig. 5).

Fig. 5.



Pedigree of variable *obscurum*.

In these three last schemes are, as said, the sub-variants left out.

I have not succeeded from *Ph. indicum* to obtain a perfectly constant luminous form, that is, one which produces no variants, though I have tried for years to do this by selection. It is evident that the conditions of culture inavoidably give cause to the rise of variants. That for the rest the faculty of varying in a very determined way, is deeply rooted in the nature of the cell, is proved by the following observations.

A few years ago Mr. FISCHER at Kiel again sent me some material of *Ph. indicum*, which had thus during many years been cultiv-

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[1]) To these relations I hope to refer at another occasion.

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ated in his laboratory. There was a considerable difference, compared to my stock, but the normal form and the two variants *obscurum* and *parvum*, I could still obtain from it as constant forms by means of colony-selection.

At the examination of numerous samples of seawater in all the seasons, taken near Scheveningen, Bergen op Zoom and den Helder, partly far from the coast [1]), I have never found *Ph. indicum* itself, but, even three times, forms which, with a broad conception of the species, might be considered as varieties of it, and else as very closely allied species. I call them *Ph. splendidum* and *Ph. splendor maris*. Short after the isolation already they produced variants, one of which is quite dark and multiplies in such a number that in cultures which are negligently re-inoculated the normal form, and with it the photogenic power, wholly disappear.

Thus, a culture at 22° C. of *splendor maris*, going out from a single phosphorescent colony, after being in 12 days six times re-inoculated on fish-broth-gelatin, produced 1800 dark variants on 22 colonies of the normal form. The culture re-inoculated six times in the same space of time on fish-agar did not yet contain any variants, whilst at the 12th re-inoculation on agar their number was also very great. The first not further re-inoculated cultures on gelatin, which accordingly had only had little opportunity to grow, after 12 days did not contain variants, in accordance with the rule that at eessation of growth no variability is manifested.

The *parvum*-variant also is in *Ph. splendidum* and *Ph. splendor maris* as distinctly recognisable as in *Ph. indicum* itself, and here too, frequently produces the primitive forms as atavists.

Basing on these experiences I think it probable, that the cause which calls forth the variants is not exclusively active in our artificial cultures, but can also be active in the sea itself, so that in this case there is a chance that dark forms, isolated from the sea will at first be taken for particular species, but after more minute observation, will prove to be variants of known phosphorescent bacteria.

By observing certain general conditions the production of dark variants can, as said, be greatly slackened, but not wholly prevented.

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[1]) Many of these samples I owe to the kindness of Dr. HOEK. Various species of luminous bacteria have been found in them to the amount of 0.1 to 5, even 7 pCt., of all present bacteria. Especially *Ph. luminosum*, and a species difficult to distinguish from it, but still quite different, *Ph. hollandiae*, occur very often. *Ph. degenerans* also is frequent.

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Among these are: strong nutrition and vigorous growth a little below the optimum temperature, free access of oxygen, such as can be attained in cultures on agar-agar, and total exclusion of the influence exerted by the secretion-products of the bacteria themselves, which is attainable by re-inoculating the young cultures very often on a new medium.

7. *Conclusion.*

I will begin with pointing to the fact that hereditary variability is a function of growth, in particular of slackened growth, but that at cessation of growth no change takes place. And furthermore that variability attacks only one independent characteristic at a time. In the sub-variant one characteristic of the normal form is partly, in the main-variant it is wholly changed. In new varieties and species more characteristics are varied.

Furthermore resuming the above given statements I come to the following conclusions. The here discussed forms of hereditary variability belong to three types: At *degeneration* all individuals, by a slow process of variability, lose their vegetative power, so that the species may cease to exist. At *transformation*, which seems to appear more seldom, all individuals lose a specific characteristic and acquire either or not another instead. At the common hereditary variability or *variation*, the normal form, probably by heterogene cell-partition, throws off some individuals, the variants, mostly differing from it by a strongly salient characteristic. The normal form itself propagates beside it quite unchanged. The variants are constant in a way corresponding with independent species; sometimes this constancy is perfect, in other cases atavists are produced, like to the normal form. Subvariants i. e. intermediate forms between normal form and variant, are less *found* than the variants themselves, but they are perhaps never wanting, and are in the same way constant as the normal forms. Whether the sub-variants are also originally *formed* in smaller number than the main variants is uncertain; what is seen is that they rapidly disappear from the cultures and are supplanted by the normal form and main variants if they are not fixed by colony-selection. Besides, each well-defined degree of variation, however slight, seems to be fixable.

The rare occurrence of the sub-variants throws some light, *First*, (by the comparison of the individual microbes with the individuals of the higher organisms) on the marked distinctness by which in higher plants and animals most varieties and species are separated, —

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for they originate by repeated variation processes, relative to different characteristics- and the chance that the common and distinctly discernable variants will partake therein and not the rare sub-variants, more difficult to distinguish, is accordingly greatest [1]).

Second, (by the comparison of the individual microbes with the tissue-cells of the higher organisms) on the no less marked confines between the tissues and the organs of one and the same individual, — for these are constituted of as many cell-variants of the embryonal cells, cell-variants, which will supplant the cell-sub-variants.

That many so-called new species will prove only variants of other species and no "good species", is not improbable. Especially in the microbes, where the want of crossing must strongly favour the prolonged continuing of the once formed variants, it is to be foreseen that in nature will often be found variants, which will long maintain themselves at their habitat. If they are isolated, the discoverer will at first be almost sure to see new species in them, and only after an accurate investigation recognise them as variants of another species.

The sub-variants of the microbes prove, that the characteristics which in the main variants are quite wanting disappear by little leaps from the normal forms. In other cases, however, the main variants seem to appear suddenly, whence it would follow, that a characteristic can also vanish at a single leap at the cell-partition; but here the sub-variants may have escaped from observation.

The variants of the microbes, regarded as cell-variants, prove that out of a cell daughter-cells may spring unlike to the mother-cell. Though the way in which this is effected is still insufficiently known, it proves the existence of heterogene cell-formation, whether by direct heterogene cell-partition (fig. 1), or, by the less probable transformation (fig. 2).

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[1]) I perfectly agree with Professor DE VRIES, that the origin of species should often be sought in the almost suddenly produced variants, or mutants, as he calls them. This is also the conclusion to which GALTON has come regarding the races, and to which he referred repeatedly since 1892, the last time, so far as I know, in Nature T. 58, pag. 247, 1898 in these words: "I have frequently insisted that these sports or "aberrances" (if I may coin the word) are notable factors in the evolution of races. Certainly the successive improvements of breeds of domestic animals generally, as in those of horses in particular, usually make fresh starts from decided sports or aberrances and are by no means always developed slowly through the accumulation of minute and favourable variations during a long succession of generations." Along quite distinct ways GALTON, DE VRIES and myself have thus arrived at the same conclusion regarding the probable origin of many races and species. But the great difficulty which lies in the explanation of the adaptions, has not been removed, neither by GALTON's „aberrants", DE VRIES' »mutants", nor my „variants".

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In order to show how decidedly heterogene cell-formation is still considered as impossible, so that it is not superfluous to afford a new evidence for its existence, I refer to the well-known book of O. HERTWIG "Die Zelle und die Gewebe", p. 64 Bd. 2, Ed. 1898, where we read as follows: „Die Theorie der heterogenen Zeugung, wo sie aufgestellt wurde, ist als grober Irthum bald beseitigt worden. So gilt als ein allgemeines Grundgesetz in der Biologie der Ausspruch „Gleiches erzeugt nur Gleiches" oder besser „Art erzeugt stets seine Art." Bei allen einzelligen Lebewesen ist erbgleiche Theilung ihres Zellenorganismus die einzige die vorkommt und vorkommen kann. Auf ihr beruht die Constanz der Art. Wenn es möglich wäre, dass bei irgend einem einzelligen Organismus die Erbmasse (Idioplasma) durch Theilung in zwei ungleiche Componenten zerlegt und auf die Tochterzellen ungleich übertragen werden könnte, dann hätten wir den Fall einer heterogenen Zeugung, den Fall der Entstehung zweier neuer Arten aus einer Art. Wie indessen alle Beobachtungen lehren, werden auch bei den Einzelligen die Arteigenschaften so streng und bis ins Kleinste überliefert, dass einzellige Pilze, Algen, Infusoriën auch noch im millionsten Gliede, ihren weit entfernten Vorfahren genau gleichen. Der Theilungsprocess als solcher erscheint daher auch bei den einzelligen Organismen nie und nirgends als Mittel um neue Arten ins Leben zu rufen."

The preceding pages prove that this view is erroneous, so that the far reaching conclusions, drawn from it in relation to ontogeny vanish at the same time.

So far there is thus no reason in contradiction with observation, which forbids admitting, that the ontogeny of the higher organisms consists in a regular course of variation processes, and that full-grown plants and animals are built up of as many cell-variants of the embryonal cells, as they contain different tissues composed of identic cells.

Botanics. -- "*On the development of Buds and Bud-variations in Cytisus adami*". By Prof. M. W. BEIJERINCK.

Cytisus adami is a hybrid between the common laburnum, *Cytisus laburnum*, and a little shrub from Styria, *Cytisus purpureus*, with purple flowers. Now and then are found on *Cytisus adami* buds

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of both species as bud-variants [1]). The experience that these buds appear in particular on older parts, and have, probably without exception, passed one or more years in dormant condition before budding and changing into the primitive forms [2]), induced me to cut down all the branches and the main stem of four specimens of *C. adami* in order in this way to excite the development of the very old buds which were, since years, in dormant condition on the old trunk. My expectation, that by these means I should obtain a great number of bud-variants, proved right: in few years I saw, together with earlier observations, appear more than a hundred buds of *laburnum* and about twenty of *purpureus*. I was thereby enabled to establish a few particularities about buds and bud-variations which follow here:

1. The ordinary axillary buds of *Cytisus adami* spring not from single cells but from cell-groups. They grow on by means of a pluricellular meristem, and not by means of one terminal cell. The latter fact was long known already and is here anew confirmed.

2. The bud-variants, also, originate from cell-groups and not from single cells, so that the cause which is active here in producing variability, must extend over many cells at a time.

That this cause is in some or other way related to unfavorable conditions of nutrition cannot be doubted.

Of course the possibility is not excluded that for *C. adami* buds and bud-variants can spring from single cells. I think this even probable as regards some of the many buds which develop from the "bud-crown" [3]). Herewith is meant the sheath of vigorously vegetating cambium-cells which is found in the callus and the bark, just in the prolongation of the procambium- or cambium-cells of truncated or thrown off buds or branches, which sheath is an active centrum for the originating of new buds. For the rest, it is not the springing forth of a bud or new individual from a single cell which is remarkable, but the fact that this can take place from an already constituted cell-group. That this really occurs, and also, that a meristem

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[1]) The word "variant" is here used in a sense somewhat different from that in the preceding paper on the variants of microbes, "component" might perhaps be more precise in this case. But I keep to the usage, as the meaning is clear.

[2]) This does not hold good for the flowers, which have no dormant period but constantly develop in the 2d year, and of which the different parts are still more subject to return to the components than the vegetative buds. But the flower may, even unreckoned the process of fertilisation, be called the organ of variability.

[3]) Translated from the German "Knospenkrone".

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constituted of many cells may be subject to the process of variation, is proved by the following observations.

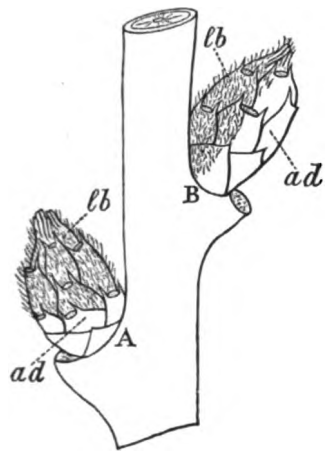

Fig. 1.

Two *laburnum* bud-variants on a branch of *Cytisus adami*; the lower bud *A* bears at its base *adami* bud-scales, but is in the higher portion pure *laburnum*; the upper bud *B* is precisely for one half *adami*, for the other *laburnum*.

At about ninety *laburnum*-buds which had developed as variants, nothing particular was to be seen, but at eight or nine were found at the base a greater or smaller number of bud-scales which could with certainty be recognised as bud-scales of *adami* (*ad* Fig. 1 A).

This observation is easy and convincing, as all parts of *laburnum*, hence the bud-scales too, are covered with silverwhite hairs, especially at the under- or back-side, while the full-grown portions of *adami* are always devoid of hairs. In all the cases, which I examined more minutely, the line of demarcation between the *adami*- and *laburnum*-portion ran in an oblique direction, so that the whole meristem belonged evidently to *laburnum*. This was constantly confirmed by the experience at the budding, as always pure *laburnum*-shoots grew from these buds.

In 1898 an extraordinarily great number of *laburnum*-variants were formed on my *adami*-trees. In consequence of the early pruning all the buds were situated low enough to be easily examined with the magnifying-glass. Two of them presented themselves as in Fig. 1 B. The line of demarcation went precisely over the middle of the bud-scales and not obliquely as in the eight cases above. The supposition that the said demarcation would also continue precisely over the middle of the meristem, proved right at the budding, for both the branches which sprung from these buds in 1899, were exactly for one half, lengthwise, *adami*, for the other half *laburnum*.

One of these "mixed branches" has attained a length of about 1 Metre, and produced more than 30 leaves with axillary lateral buds, of which about 15 belonged to *laburnum*, the other 15 to *adami*. At its extremity was in the autumn of 1899 an open "summer-bud", still for one half *adami*, for the other half *laburnum*; this summer-bud was not closed with bud-scales, and died in the winter of 1899—1900.

The second branch has become about $^1/_2$ M. long, and bore more

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than 12 leaves with axillary buds, again belonging for one half to *laburnum*, for the other to *adami*. In the autumn of 1899 a closed „winter-bud" with bud-scales was formed at the extremity. Though the line of demarcation seemed also to go over the middle of this terminal bud, a *laburnum*-branch developed from it in the summer of 1900, which only at the base bore some *adami*-leaves, so that the separation within the bud must have run obliquely and divided the meristem into a larger *laburnum*- and a smaller *adami*-portion.

This description proves that the two halves of the „mixed branches" have each grown from an independent half of the meristem, which half cannot consist of less than one cell, so that the continued growing of the branches with one terminal cell is out of question, accordingly it is certain that the branches of *Cytisus adami* grow with at least 2, and probably many more meristem cells.

The two separating lines between *laburnum* and *adami* which are seen over the full length of the „mixed branches", easily discernible on the bark as the confines between a portion set with hairs and another without, ran in 1899 for the greater part of course between the leaves, but in some places also through the leaves themselves. Some of these „mixed leaves" were situated exactly for one half on the *laburnum*- for the other on the *adami*-portion of the branch. In this case the trifoliate leaf was as exactly for one half an *adami*- and for the other a *laburnum*-leaf, and over the whole length of the petiole and the midrib of the terminal leaflet the line of demarcation was distinctly discernible. This would, if necessary, be sufficient to prove that also each leaf takes birth from at least two, and probably more meristem cells. But the pluricellular origin of the leaves of the higher plants has, so far as I know, never been called in question, though this has been the case concerning the origin of the lateral buds.

So, it was of importance to establish whether the axillary buds of these „mixed leaves", exactly placed on the confine, would likewise produce „mixed branches", by which the question would be answered if one bud might spring forth from two or more cells at a time. The answer was not dubious: all the buds, placed in the axils of the leaves, which were for one half *laburnum*, for the other *adami*, produced, in the summer of 1900, as well *laburnum*- as *adami*-leaves, and in this case, too, some leaves again were mixed, namely partly *adami*- partly *laburnum*-leaves.

In most cases the line of demarcation went very obliquely through the "mixed buds" of this second generation, so that the whole meristem early in the year consisted of only *adami* or only

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laburnum. In one of these buds however the boundary line went precisely through the middle, but this bud contained an inflorescence of which the summit had died off in the winter of 1899—1900. At the base were however pure *laburnum*- and pure *adami*-flowers, and one flower was precisely for one half *laburnum*, for the other *adami*, so that also flowers evidently spring not from one cell, but from a cell-group.

The preceding description proves that in the springing forth of the *laburnum*-variant from *Cytisus adami*, as well a whole meristem may be concerned as half of it, and that the cause which gives rise to the appearance of a bud-variant is active when the meristem is completely formed, and not in the far-back moment when the cell-group, which later manifests itself as a meristem, was still a single cell. For if this were the case it could not be possible that a portion of the bud, which produces the variant, continued to belong to *C. adami* itself.

Hence it follows that the bud-variant is not produced by variation of a single cell but by that of a cell-group.

Fig. 2.

One year's *purpureus*, *ps*, sprung as a bud-variant, from a dormant *adami*-bud, at the extremity of a "short-shoot" *ad*. On the left a "long-shoot" of *adami*, at the extremity of a "short-shoot".

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To show that also the *purpureus*-variant is produced by the variation of an already constituted *adami*-meristem, and not of a single cell, far-back in the evolution of that meristem, I refer to Fig. 2.

Here we see a one year's *purpureus*-shrub (*ps*) placed at the extremity of a "short-shoot" of *Cytisus adami* [1]). Commonly the *purpureus*-variants, quite like those of *laburnum*, spring from com-com buds, whence the exact moment of their birth is not clear. But the peculiarity of the case figured here is that the "short-shoot", terminating in *purpureus*, had already grown for a number of years as *adami*, and that consequently it is not possible to doubt, that *purpureus* has come forth from the whole *adami*-meristem. As this meristem is pluricellular, the cause, which led to produce the *purpureus*-variant, must thus also have affected a cell-group and not have been confined to a single cell.

In a few cases the *purpureus*-bud was not found alone, but also some *adami*-buds of the nearest surrounding were changed into *purpureus*. So, this summer, in my garden, of six quite independent, dormant, three years' buds at the summit of a "long shoot" of *Cytisus adami*, separated from each other by relatively short internodes of the long-shoot, no less than four are changed into *purpureus*, and besides, the two unchanged *adami*-buds are placed between the higher and lower situated *purpureus* branchlets. Accordingly the influence which caused the variation must have been active simultaneously in four meristems, the distances between which, at the time of the variation, must certainly have amounted to some tenth parts of millimeters.

Herewith I think to have made good the two statements expressed at the beginning of this paper, and I only wish to add that already before, but at quite another occasion (*Cécidiogénèse du Cynips calicis*. Archives Neêrlandaises, Sér 2, T. 2, 1897, pag. 436), I came to the opinion that variability, though habitually going out from a single cell, is not necessarily always bound to it, but sometimes has a cell-group as starting point, so that there can be question of uni- and pluri-cellular variability.

The relatively great number of bud-variants of *adami*, which I have examined, consisted, as usually, only of pure *laburnum*- and pure *purpureus*-branches. Hybrids, in which both factors occur, but one preponderant as compared to its part in *adami*, seem never to be produced. Still I believe that in the cell-layers of the bud-

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[1]) A "short-shoot" consists of a closely crowded succession of nodes, between which the internodes are not developed; they grow very slowly and point to unfavorable conditions of nutrition.

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meristem, which form the separation between *adami* and one of the variants, there must occur transitory cells, which, could they be independently developed and cultivated into new individuals, would produce such derivated hybrids. Perhaps the "supplanting" of these transitory cells by the completely varied cells, may be compared to the rarity (discussed in the preceding paper on the variants of microbes) of the sub-variants as compared to the normal form and the main variants, by which it seems possible to explain, on the one hand the existence of distinctly marked bounds between the species, on the other hand, the not less marked bounds between the different organs and tissues of the higher organisms.

Physiology. — "*On the permeability of the red bloodcorpuscles for NO_3- and SO_4-ions*". By Dr. H. J. HAMBURGER.

The question whether cells are permeable for certain substances and if so, to what extent, is not only important for our knowledge about metabolic and other vital processes, but is also of great importance from a pharmacological point of view. Here again the red bloodcorpuscles are found to be the favourable test-objects to study this question accurately. It is only natural that these cells are in this case equally serviceable as in many other problems of a general scope. In the first place they are met with in the isolated condition (in contrast with most other cells) and they can therefore be procured without being injured; in the second place the influence of different agencies can in them be better traced than in other cells, thanks to their change of form and dimension as well as to the extrusion of red colouring matter, and in the third place the reciprocal influence between the contents of the cell and its natural surroundings can be studied in detail by chemical analysis.

It is through the study of the laws of the isotonic coëfficients (HUGO DE VRIES) of the red blood-corpuscles that the problem of permeability was first brought into the foreground [1]).

I will not here enlarge on what has hitherto been investigated and written on this subject. I only wish to point out that it has been agreed that there are: 1°. substances which penetrate through the bloodcorpuscles and destroy them (for instance NH_4Cl); 2° sub-

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[1]) HAMBURGER, De permeabiliteit der roode bloedlichaampjes in verband met de isotonische coëfficienten. Versl. en Meded. d. Kon. Akad. v. Wetensch., 1890, bl. 15.

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stances which permeate them, but are harmless (for instance urea); whereas there is a great number of substances, amongst others salts as $NaCl$, Na_2SO_4 etc., which are likewise harmless, but concerning whose permeating capacities opinions differ.

Some assert that alkali-salts as such can penetrate into the blood-corpuscles, others say that they are absolutely impenetrable to these salts.

Formerly I agreed with the former opinion; now I am convinced, considering the theory of the electrolytic dissociation, that the truth lies half-ways and that the bloodcorpuscle is not permeable for the alkali-salt as such, nor for the metal-ion either, but for the acid-ion.

When CO_2 is mixed with blood the following symptoms will be observed: the bloodcorpuscle becomes richer in chlorine, richer in water and poorer in alkali. The serum undergoes just the reverse change, an exchange of substances has thus taken place.

The *kalium-* and *natrium*-contents of blood-corpuscle and serum have nothing to do with this, these are unchanged (GÜRBER).

There is now no difficulty in explaining these symptoms.

Through the influence of CO_2 carbonate appears in the blood-corpuscles. A part of the bivalent electronegative CO''_3-ions leaves the bloodcorpuscle and is replaced by the double number of electro-negative Cl'-ions. Therefore increase of the Cl-contents of the blood-corpuscles and increase of the alkali-contents of the serum.

As two Cl'-ions are needed to replace one CO_3''-ion and every ion, be it mono- or bivalent, represents the same power to attract water (osmotic pressure), the power of water-attraction in the bloodcor-puscle-contents must increase more than that of the serum and the bloodcorpuscle attracts water, it swells.

The following experiment confirms this proposal.

The serum is removed as thoroughly as possible from defibrinated blood and the bloodcorpuscles are then washed with a solution of glucose, until all the serum has been removed. The intracellular liquid now reacts neutrally. The passing of CO_2 through the fluid suspension of the bloodcorpuscles in glucose does not make the liquid alkaline, although the bloodcorpuscles have taken in CO_2, and K_2CO_3 has been formed; *but as such it does not extrude.* CO_3 however can leave the bloodcorpuscle, provided an equivalent quantity of another ion of the same name takes its place. Thus, when the glucose-solution is substituted by a $NaCl$-solution isotonic with the bloodcorpuscles, the latter becomes immediately alkaline and the bloodcorpuscles swell. The reason is this that CO_3''-ions have left the bloodcorpuscles and the double number of Cl'-ions have taken their place. The

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kalium and natrium of the bloodcorpuscles and surrounding have in the meantime remained unchanged.

The question may now be considered what the result will be, when in a suspension of bloodcorpuscles in glucose not a solution of Na Cl is added, but a solution of $NaNO_3$ isotonic with the bloodcorpuscles. Then the $NaNO_3$-solution also becomes *alkaline* through natrium-carbonate, very weak when no CO_2 was made to pass through the suspension, but pretty strong when this had been the case. And in accordance with what is observed in Na Cl, swelling is also found here after addition of the isotonic salt-solution to the CO_2-suspension of the bloodcorpuscles in glucose-solution. This is self-evident, for, when it is admitted that $(NO_3)'$-ions enter the bloodcorpuscles and CO_3''-ions extrude, then every CO_3''-ion which extrudes must be replaced by two $(NO_3)'$-ions, and as one $(NO_3)'$-ion represents the same osmotic pressure as one CO_3''-ion, the power of the bloodcorpuscle to attract water (osmotic pressure) must increase and the latter will swell.

If the experiment is performed with Na_2SO_4-solution, then this solution will likewise be seen to become alkaline, weak, when no CO_2 was mixed with the suspension of the bloodcorpuscles in glucose-solution, rather strong when this had been the case. The volume of the bloodcorpuscles did not increase however. This is evident; against one SO_4''-ion which enters the bloodcorpuscles, one CO''_3-ion extrudes; the power of water-attraction of the bloodcorpuscles-contents remains the same during this exchange.

From these experiments the conclusion may be drawn that the red bloodcorpuscles are permeable for NO_3'- and SO_4''-ions; which was hitherto not accepted even by those who did not doubt a permeation for chlorine, as based upon direct quantitative analysis.

Meanwhile our conclusions in regard to the permeability of the red bloodcorpuscles for SO_4- and NO_3-ions, also find their confirmation in direct quantitative chemical analysis of the added sulphate and nitrate before and after the mixture with the bloodcorpuscles.

Not for all acid-ions however quantitative chemical analysis can be performed with sufficient accuracy required for the purpose.

For such cases we now find in the described method a means which enables us to judge about the permeability of the bloodcorpuscles for such ions. It only requires to be noted whether alkaline reaction appears, or if already present, increases, in the bloodcorpuscles washed with glucose, after addition of the salt-solution containing the ion which must be examined. A preceding treatment of the suspension

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of bloodcorpuscles in glucose-solution with CO_2 is much to be recommended, as the number of CO_3-ions in the bloodcorpuscles increases thereby and therefore a better opportunity offers itself for the acid-ions (anions), which are to be examined, to change places with CO''_3 and to enter. Consequently the alkaline reaction of the solution about to be examined will become stronger. That CO_2 is able to promote the entrance of ions into cells seems to me of great importance for the economy of the human body.

(November 21, 1900.)

E R R A T A.

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		„	31	„	Aa	„	aA'
		„	31	„	aA'	„	aA''
		„	32	„	aB'	„	aB''
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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday November 24, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 24 November 1900 Dl. IX).

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The following papers were read:

Chemistry. — "*Review of the results of a comparative study of the three dinitrobenzenes.*" By Prof. C. A. LOBRY DE BRUYN.

(Read October 27, 1900).

As the comparative investigation of the three dinitrobenzenes, which was started some considerable time ago and the results of which have already been partly published [1]), has now practically been brought to a close, a short and systematic review of the prin-

[1]) Rec. 2. 205, 236, 238. 13. 101. 15. 85. 18. 9. 13. Ber. 24. 3749.

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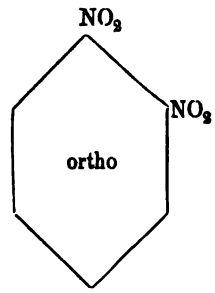
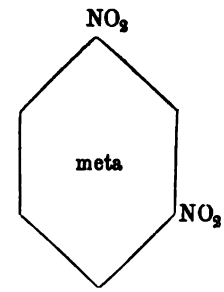
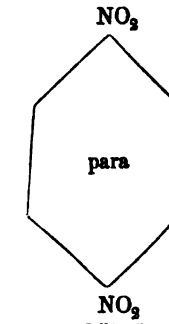
cipal results may be given. The particulars of the part which is not yet published will appear fully in the "Recueil".







melting point	116°.5	89°.72 (Mills)	172°.1
specific gravity	1.59	1.575	1.625
boiling point	319° (773.5)	302°.8 (770.5)	299° (777)

The specific gravities increase with the melting points; o-dinitrobenzene has the highest, p-dinitrobenzene the lowest boiling point.

The solubilities decrease with the rise of the melting points; this applies to all of the ten solvents employed. The three dinitrobenzenes like most isomeric substances, behave therefore conform to the rule of CARNELLEY and THOMSON which states that of two or more isomeric bodies those with the highest melting points show the smallest solubility and *vice versa*.

The heat of combustion of the three isomers has already been determined in 1891 by BERTHELOT and MATIGNON with samples taken from my preparations [1]). It has been shown that this is largest for orthodinitrobenzene and smallest for paradinitrobenzene.

The following tables show the different behaviour of the three isomers towards reagents.

AQUEOUS ALKALIS.

Ortho.	Meta.	Para.
Quantitatively in $o.C_6H_4NO_2.ONa + NaNO_2$ LAUBENHEIMER [2])	Chief reaction: reduction to m.m. dinitroazoxybenzene oxydation to oxalic acid. Brown amorphous substances and H_3N as bye-products.	Almost quantatively in $p.C_6H_4NO_2.ONa + NaNO_2$, very little p.p. dinitroazo- and azoxybenzene.

[1]) C. R. **113**. 246.
[2]) Ber. **9**. 1826.

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ALCOHOLIC AND METHYLALCOHOLIC SODIUM.

Ortho.	Meta.	Para.
Quantitatively in $o.C_6H_4NO_2.OCH_3(OC_2H_5) + NaNO_2$	For the greater part in $O_2N\text{-}C_6H_4\text{-}N\text{-}N\text{-}C_6H_4NO_2$ (O) MICHLER [1]), KLINGER en PITSCHKE [2])	Quantitatively in $p.C_6H_4.NO_2.OCH_3.(OC_2H_5) + NaNO_2$

ALCOHOLIC AND AQUEOUS AMMONIA.

Ortho.	Meta.	Para.
Quantitatively in $o.C_6H_4.NO_2.NH_2$ LAUBENHEIMER [3]).	No action up to 250°.	$p.C_6H_4.NO_2.OCH_3.(OC_2H_5) + p.C_6H_4NO_2.NH_2$ in varying proportions.

HALOGENS.

Ortho.	Meta.	Para.
chlorine. $o.C_6H_4Cl_2$ little, or no $C_6H_4Cl.NO_2$	m. $C_6H_4Cl.NO_2$ and m. $C_6H_4Cl_2$	Exclusively p. $C_6H_4Cl.NO_2$
bromine. $o.C_6H_4Br.NO_2$ and $C_6H_4Br_2$ etc.	Same as ortho.	p. $C_6H_4Br.NO_2$
iodine. $o.C_6H_4I.NO_2$	m. $C_6H_4I.NO_2 + C_6H_4I_2$ etc.	p. $C_6H_4I.NO_2$

HYDROCHLORIC (and Hydrobomic) ACID.

Ortho.	Meta.	Para
o. $C_6H_4Cl_2$ o. $C_6H_4Br_2$	m. $C_6H_4Cl_2 + C_6H_3Cl_3$	p. $C_6H_4Cl_2$

SODIUM MONOSULPHIDE.

Ortho.	Meta.	Para.
1 mol. to 1 mol. of Na_2S: $C_6H_4NO_2.SNa + NaNO_2$ 2 mols. to 1 mol. of Na_2S: $O_2NC_6H_4\text{-}S\text{-}C_6H_4NO_2 + 2NaNO_2$	Chief product: $O_2NC_6H_4\text{-}N\text{-}N\text{-}C_6H_4NO_2$ (O) $+ Na_2S_2O_3$ besides brown, amorphous substances.	Chief product: $O_2N\text{-}C_6H_4\text{-}N:NC_6H_4NO_2$

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1) Ber. 7. 423.
2) Ber. 18. 2551.
3) Ber. 11. 1155.

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AMMONIUM SULPHIDE.

Ortho.	Meta.	Para.
$C_6H_4 . NO_2 . NH_2$ [1]) $O_2N\,C_6H_4\,S\text{-}C_6H_4NO_2$ $O_2N\,C_6H_4\,S\text{-}S\text{-}C_6H_4NO_2$	Chief product: $C_6H_4NO_2 . NH_2$ (HOFMANN. MUSPRATT.)	Chief product: $C_6H_4NO_2 . NH_2$ [1])

SODIUM DISULPHIDE. [2])

Ortho.	Meta.	Para.
Quantitatively in $O_2N\,C_6H_4\text{-}S\text{-}S\text{-}C_6H_4NO_2$ $+ 2\,NaNO_2$	Quantitatively in $O_2N\text{-}C_6H_4\text{-}N\text{-}N\text{-}C_6H_4NO_2$ (O) $+ Na_2S_2O_3$	Quantitatively in $O_2N\,C_6H_4\text{-}N : N\text{-}C_6H_4NO_2$ $+ Na_2S_2O_3$

POTASSIUM CYANIDE IN AQUEOUS SOLUTION.

Ortho.	Meta.	Para.
Reduction to amorphous products. A good deal of o. $C_6H_4.NO_2 . OH$ and HCN	Dark amorphous reduction products CO_2, H_3N and nitrite.	Reduction to $O_2N\text{-}C_6H_4\,N\text{-}N\text{-}C_6H_4NO_2$ (O) also KCNO which yields ammonium carbonate.

SOLUTION OF POTASSIUM CYANIDE IN ALCOHOL OR METHYL ALCOHOL.

Ortho.	Meta.	Para.
No action up to 170°. Tarry products at higher temperatures.	Nitrile of nitromethyl-(ethyl)salicylic acid: $C_6H_3O\,CH_3(C_2H_5) . CN.NO_2$ 1. 2. 3. besides amorphous reduction products and KNO_2.	On boiling, chiefly $C_6H_4NO_2 . OCH_3(C_2H_5)$ $+ HCN + KNO_2$ Trace of azoderivative.

VELOCITY OF SUBSTITUTION OF THE NO_2-GROUP BY OC_2H_5 AND OCH_3 [3]).

	$NaOC_2H_5$		$NaOCH_3$	
	Ortho	Para	Ortho.	Para
25°	0,0260	0,211	0,0170	0,0442
35°	0,0786	0,707	0,0484	0,143
45°	0,233	2,21	0,139	0,474
	1 : 8.1 à 9.5		1 : 2,6 à 3.6	

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[1]) RINNE and ZINCKE Ber. 7. 869. 1372. — KÖRNER Gazz. chim. 1874.
[2]) BLANKSMA. Rec. 19. 121. Proc. Royal Acad. of Sc. of Amst. Nov. 1899.
[3]) ALPH. STEGER. Rec. 18. 13.

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The close. examination of this review gives rise to the following remarks.

It is ,only towards hydrochloric acid and the halogens [1]) that the three isomers behave in the same way; in all three, chlorine (bromine) is substituted for the NO_2-group. But as regards Cl (Br) the ortho-derivative differs from the para-compound in so far that both its NO_2-groups are replaced by chlorine or bromine whilst in the latter only one NO_2-group is acted on; with the meta-compound the dichloro- and nitro-chloroderivative have been obtained.

Moreover the meta-isomer always behaves differently from the ortho- and generally also from the para-isomer. These latter, therefore do not always behave identically, or similarly. They do so in the case of aqueous and alcoholic alkalis which readily cause substitution for one of the nitro-groups, whilst with meta-dinitrobenzene a reduction to the azoxy-compound takes place. A difference exists in the behaviour of ortho- and para-dinitrobenzene towards ammonia; whilst the ortho-isomer readily yields nitraniline at a low temperature, this is formed with difficulty from the para-compound at a higher temperature together with the corresponding nitro-oxyalkyl. The latter is formed in greater quantity when the concentration of the H_3N becomes less. It seems to me that from these observations the conclusion may be drawn that alcoholic ammonia does not only contain the H_3N mol. but also the H_4NOCH, or $H_4NOC_2H_5$ molecule.

Na_2S and Na_2S_2 act on the ortho-dinitrobenzene and form the substitution products nitrothiophenol or the mono- or disulphide whilst the two other dinitrobenzenes are reduced. It is a peculiar fact that meta-dinitrobenzene is reduced to the azoxy- and para-dinitrobenzene to the azo-compound, whilst in the second place attention must be called to the circumstance that when applying Na_2S_2 the reductions take place quantitatively [2]). That $Na_2S_2O_3$ is also formed when Na_2S is used, points to the intermediate production of Na_2S_2.

The action of ammonium sulphide on ortho dinitrobenzene has now become quite clear; $(H_4N)_2S$ acts by reduction and substitution; the liberated sulphur then forms $(H_4N)_2S_2$, which gives rise to the disulphide by direct substitution.

Potassium cyanide in aqueous solution causes reduction and is

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[1]) Also partly towards ammonium sulphide.

[2]) Na_2S_2 as a deoxidising agent will be further investigated.

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itself oxidised to potassium cyanate which of course, yields immediately H_3N and CO_2. It is by no means such a handy deoxidising agent as Na_2S_2. Only in the case of para-dinitrobenzene, was the azoxy-compound obtained as a properly crystallisable product; in the case of the two other isomers brown amorphous substances are formed; the ortho-compound yields a decided quantity of nitrophenol owing to KOH being set free by hydrolysis.

The action of potassium cyanide in alcoholic solution is of much more importance. It is first of all remarkable that it does not act on ortho-dinitrobenzene whilst it behaves towards para-dinitrobenzene as if its solution were dissociated into $KOCH_3(C_2H_5)$ and HCN. This difference in behaviour is not easy of explanation. In the second place, the behaviour of meta-dinitrobenzene is interesting. The formation of the two substances $C_6H_3.OCH_3(C_2H_5).CNNO_2$ 1.2.3. may be best explained by assuming that the CN-group first takes up a position between the two NO_2-groups (while H and K reduce another portion) whilst further on one of the NO_2-groups is replaced by oxyalkyl owing to the formation of potassium alcoholate.

An account of the researches of Dr. A. STEGER on the substitution velocity of a nitro-group in ortho- and para-dinitrobenzene by an oxyalkyl and the peculiarities observed has already been given [1]).

Chemistry. — "*The* WESTON-*cadmium cell.*" By Dr. ERNST COHEN. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Read October 27, 1900).

1. In a paper on this cell (compare this vol. p. 217—228) it was stated that cadmium amalgam with 14.3 per cent of cadmium may occur in two forms which pass into each other at 23° C. The existence of these forms was assumed on two grounds:

1st. From the fact that the E.M.F. of cells, constructed according to the scheme Cd-dilute solution of cadmium sulphate-Cd amalgam with 14.3 per cent of Cd, is not always the same function of the temperature but that this function may be represented by the curves shown in the subjoined figure at I, III and at II.

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[1]) Proc. Royal Acad. of Amsterdam. Oct. 29, 1898.

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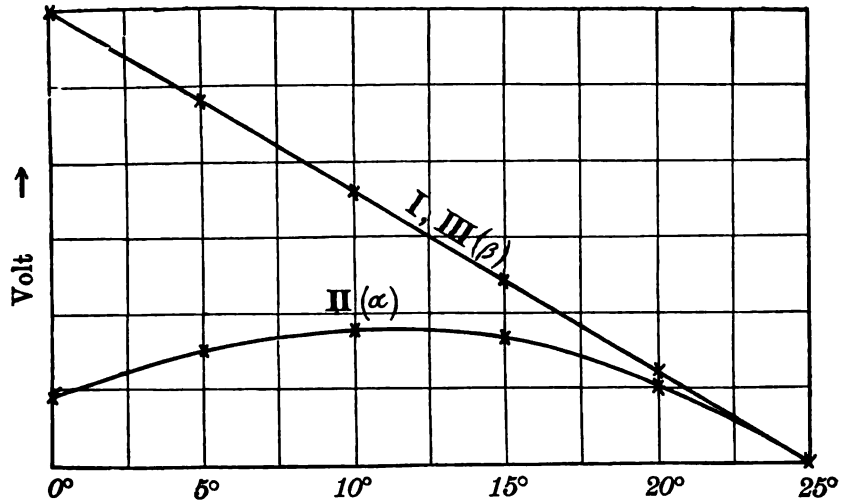

Fig. 1.

2nd. From the fact that the amalgam of the cells which follow the curve I, III showed a strong contraction in the dilatometer at 0° C.

The amalgam of the cells I, III was called by me the metastable (below 23° C.), that of the cell II the stable one.

Dr. W. BÖTTGER of Leipsic has now been so kind as to call my attention to the fact that the idea about the supposed metastability of the amalgam of the cells I, III is incorrect.

That this cannot really be correct may be shown as follows. If two cells for instance I and II of the previous paper, are linked in opposition (see fig. 2), and it is assumed that the E.M.F. of the cell with the metastable amalgam is greater than that with the stable one (at a certain temperature below 23° C.), then as in both cells the amalgam-electrode forms the positive pole, metallic cadmium would be deposited on the passing of the current, at the Cd-pole in II; *stable* cadmium amalgam would therefore pass into solution in II, whilst metallic cadmium would dissolve in I while *metastable* amalgam was being formed.

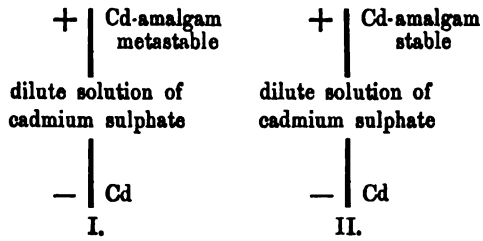

Fig. 2.

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The result, therefore, would be that (below 23°) the *metastable* system would form at the expense of the *stable* one by electrical action and this, according to known principles, is impossible.

Dr. BÖTTGER is, therefore, right when he says that the curve I, III (in fig. 1) relates to the stable and the curve II to the metastable cadmium-amalgam and that consequently according to the *electrical* measurements, the cells of JÄGER should have contained *stable* amalgam.

2. Against this result obtained by electrical means stands the result furnished by the dilatometer, which shows that the amalgam of the cells I and III, (which according to the electrical measurement ought to be stable) is not in equilibrium at 0° C. and undergoes a change accompanied by contraction.

I cannot at this moment reconcile these two apparently contrary results, but hope that the researches of Mr. H. C. BIJL on the behaviour of cadmium-amalgams will throw light on this subject.

3. Meanwhile another new contradictory matter arises, which has been duly pointed out to me by Dr. BÖTTGER.

If the cell II contains the metastable amalgam as positive pole, then a WESTON-cell constructed with this amalgam as negative electrode (IIa of the previous communication) must possess an E.M.F. which is smaller than those of the cells (Ia and IIIa), which contain the stable amalgam as negative electrode.

The measurement however, gave as result that IIa has actually a greater E.M F. at 0° C. (1.0231 Volt) than Ia and IIIa (1.0197 Volt).

Actual repetition and extension of these investigations will only be possible when we know the circumstances during which the metastable amalgam is produced, namely when the researches on the behaviour of the cadmium-amalgams shall have been practically brought to a close.

On account of these contradictory facts I desire to postpone for the present any further conclusions as to the suitability of the WESTON-cell.

Amsterdam, October 1900.
Chem. University Laboratory.

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Physiology. — Prof. C. A. PEKELHARING "*On the proteids of the glandula thymus*".

Some time ago I have in this place given an account of certain researches concerning the fibrin ferment, which led me to the conclusion that this enzym should be looked upon as a nucleoproteid, in this sense, that nucleoproteids of different origin, are capable of inducing the formation of fibrin out of fibrinogen, nucleoproteids from the thymusgland and the testis, as well as from the cells that are suspended in the blood.

These substances however only become an active fibrin ferment, when they have had the opportunity to form a combination with lime.

On various grounds I supposed that the fibrin ferment should yield lime to the fibrinogen for the formation of fibrin. I can however no longer hold this view, since HAMMARSTEN has proved, that fibrin, when it is prepared in the highest possible degree of purity, contains so little lime, that this substance cannot be considered to be a lime-combination. Moreover I have convinced myself of the accuracy of HAMMARSTEN's criticism by my own experiments. It cannot be said that fibrin is a lime combination and originates by the fact of lime passing from the ferment into the fibrinogen.

Meanwhile this does not alter my opinion about the nature of the ferment. This opinion is yet further confirmed by a research by Mr. HUISKAMP about the proteids of the glandula thymus, of which the full description will soon appear.

It is well-known, that out of thymus, by extraction with water, two nucleoproteids can be obtained of which one has been specially studied by LILIENFELD, who has given to it the name of nucleohiston.

Mr. HUISKAMP now found that the nucleohiston as well as the other nucleoproteid can form compounds with calcium, of which the solubility in water depends upon the greater or smaller quantity of salts of alkali or alkalic-earths, which it contains. Nucleohiston is quite insoluble, the other nucleoproteid incompletely soluble in water, which contains 0.1 to 0.5 pCt. chloride of calcium, but by increasing the amount of lime-salt of the fluid, or by adding other neutral salts, both proteids dissolve easily.

The substances that are precipitated from an extract of the thymus by the addition of the necessary quantity of chloride of calcium are to be considered as salts of calcium, in which the nucleoproteid

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plays the part of an acid. They can be decomposed by acetic acid; then the proteid is left behind as a substance insoluble in water.

By treatment of these compounds of proteid and lime with oxalate of kalium, oxalate of calcium and the kalium-compound of the nucleoproteid is formed. The latter is like the natrium- and ammonium-compound easily soluble in water. The magnesium and the baryum-compound however are just as the calcium-compound hardly soluble in pure water, but they *do* dissolve in water, to which a very small quantity of ammonia is added. The alkali- as well as the alcalic earths compounds of the nucleohiston are precipitated from the neutral or extremely weak alkalic solution by the addition of so much salt, that the fluid e. g. for Na Cl contains 0.9 pCt., for K Cl 1.13 pCt., for $CaCl_2$ and for $CaCl_2$ 0.1 pCt., for $MgSO_4$ 0.2 pCt. The other nucleoproteid can be precipitated, always incompletely however, by the salts of alkalic earths, namely by the addition of salts so that the concentration is the same as for the precipitation of the nucleohiston; by alkalisalts it is not precipitated.

Mr. HUISKAMP succeeded in preparing both proteids each separately, with great purity. The results of the elementary analysis of the different preparations, which very well agreed, proved this.

The composition of the lime-compounds appeared to be thus:

	C.	H.	N.	P.	S.	Ca.
Ca-nucleohiston	45.3	6.5	17.1	3.75	0.51	1.34
Ca-nucleoproteid	49.8	7.3	15.9	0.95	1.19	1.34

Either lime-compound now can act as a fibrin ferment. The investigation on this point brought to light that this ferment action is influenced by the amount of lime salt of the fluid, in which the fibrinogen and the ferment are dissolved and in such a way, that the action is most powerful, when the solution contains 0.1 à 0.5 pCt. $CaCl_2$, namely with such a concentration, by which either nucleoproteid is least soluble in fluids, which contain hardly any other salt. When the precipitate, obtained by adding to a pure solution of one of the nucleoproteids, which contains little salt, so much $CaCl_2$, that the fluid contains 0.1 pCt. of this salt, is mixed with a solution of fibrinogen in chloride of natrium, it is dissolved readily. This solution coagulates in the quickest and most complete way, whenever so much chloride of calcium is added to it, that the amount of that substance is again brought to 0.1 pCt.

When the amount of $CaCl_2$ reaches 0.5 pCt., the coagulation is

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already incomplete, when it comes near to 1 pCt., the coagulation does not take place.

A few years ago HORNE [1]) has found, that the coagulation of blood can be interfered with or quite prevented, by mixing it with a solution of calcium-, strontium- or baryumchloride, in such a way, that the mixture contains 0.5 pCt. of the added salt.

Mr. HUISKAMP, before he was acquainted with HORNE's result, had come to the same conclusion, at least with regard to chloride of calcium and baryum. He has investigated, whether also the nucleoproteid of the bloodserum, the fibrin ferment *sensu strictiori*, just as the nucleoproteids of the thymus, depends in its action on fibrinogen upon the amount of lime-salt contained in the fluid and he has received an affirmative answer to that question.

The substance was prepared in the way, before described by me, by treatment of the diluted bloodserum with acetic acid and, dissolved in water, with the aid of very little ammonia. Now it appeared, that out of this solution this nucleoproteid could also be precipitated by chloride of calcium and here also in the most satisfactory way, when the amount was brought to 0.1 pCt.

Now 900 cc. oxblood fresh from the animal were mixed with 100 cc. 10 pCt. $CaCl_2$. The blood, which now contained 1 pCt. $CaCl_2$ (apart from the salts already present in it) did not coagulate and was centrifugated. The plasma showed a slight beginning of coagulation, when it was diluted with $^2/_3$ of its volume of water, but coagulated completely in a quarter of an hour's time, when it was diluted with 3 parts of water, by which the amount of $CaCl_2$ was reduced to 0.25 pCt., a concentration, which causes the lime-compound of the nucleoproteid to be insoluble, at least when no other salts are present in a quantity worth mentioning.

Some time ago I have communicated in this meeting, that magnesium-sulphate can prevent the coagulation of the blood by interfering with the combination of nucleoproteids with lime. Mr. HUISKAMP now found that chloride of baryum acts in the same way but yet more strongly. When blood is added to a solution of $BaCl_2$, the baryum combines with the nucleoproteid; in consequence of this the coagulation is prevented and the plasma, separated by means of the centrifuge, does not coagulate spontaneously, not even after being diluted with water, but it does so, when not only the amount of $BaCl_2$ is reduced by diluting with water but also the amount of lime is increased by the addition of $CaCl_2$. This plasma again

[1]) Journal of Physiol., Vol. XIX, p. 356.

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coagulates in the quickest and most complete way, when after dilution with water, the amount of $CaCl_2$ is brought from 0.1 to 0.5 pCt. When yet more lime-salt is added, so that by this alone without the aid of other salts; the nucleoproteid-lime-combination might be dissolved, then the coagulation does not take place at all.

The arguments which I have on a former occasion brought forward in order to defend the view, that the nucleoproteids themselves and no admixtures, act, with the aid of lime, as a fibrin ferment, have been confirmed, I think, by the investigation of Mr. HUISKAMP. Chloride of calcium influences the action of ferment, at those very degrees of concentration, which render it capable of altering the state of the nucleoproteids.

The supposition, that that influence should be in relation with perfectly unknown admixtures, which should occur in the now very purely prepared nucleoproteids of the thymus, is, I think, not confirmed by a single observation.

The supposition, suggested by SCHÄFER [1]), in connexion with HORNE's results, that the interference with the coagulation by calcium-, strontium- and baryumsalts is founded on the capability of salts of dissolving fibrin, is disproved by the observations of numerous investigators, also by those of Mr. HUISKAMP, from which it is evident, that a corresponding quantity of chloride of natrium does not bring about any delay or incompleteness of the coagulation.

Botanics. — "*Contributions to the knowledge of some undescribed or imperfectly known Fungi*" (4th Part and end) [2]). By Prof. C. A. J. A. OUDEMANS.

† † MELANCONIEAE.

α. Hyalosporae.

GLOEOSPORIUM Desmazières et Montagne.

Fig. 2.

Gl. Aucubae Oud. Upper face.

85. GLOEOSPORIUM AUCUBAE Oud. n. sp. — On the leaves of *Aucuba japonica*. — Bussum, July 1900. — Mr. C. J. KONING.

Epigenum. In foliis necatis nigrefactis globuli vel cirrhi subtilissimi, dilute straminei, conspicui fiunt, qui, orificia epidermidis minima obturantes et e cavernulis infra-epidermoidalibus, 500 μ latis,

[1]) Textbook of Physiol., I, p. 170.

[2]) For 3rd Part see these Proceedings p. 332.

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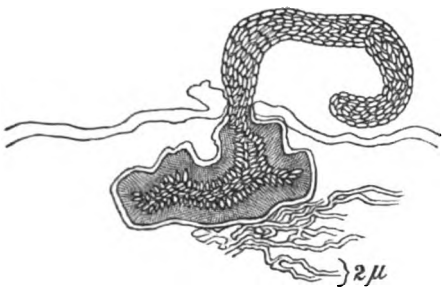
Fig. 3.



id. on vertical section.

200 μ altis, propulsi, statimque coagulati, ex mere conidiis consistunt. Sunt haec conidia elliptica vel parum oblongata, 4—7× 2—3 μ, hyalina, continua, biocellata, basidiisque acicularibus, 35 μ altis, e strato proligero fuligineo oriundis, fulciuntur.

Fig. 4.

id. Basidia with conidia and conidia separately.

*Gloeosporium antherarum Oud. n. sp. N. K. A. 3, I, 506 and Hedw. XXXVII (1898) p. 179. — On weakened anthers of Calystegia sepium. — Leimuiden, July 1894; Mr. L. Vuyck.

MYXOSPORIUM Link.

*Myxosporium Coryli Oud. n. sp. N. K. Arch. 3, I, 507 and tab. VI f. 10. — On branches of *Corylus Avellana*. — Nunspeet, March 3, 1898; Mr. Beins.

86. Myxosporium juglandinum Oud. n. sp. — On the branches of *Juglans regia*. — Scheveningen, 1894.

Pustulae prominentes, sub peridermate occultatae, tandem, peridermate irregulariter rupto, hiantes glebulamque griseam exponentes. Continet haec conidia fusiformia, hyalina, continua, ad polos anguste rotundata, biocellata, 8—10×2—2$^1/_3$ μ, primitus basidiis tenerrimis, 20—25×1 μ, suffulta. Differt a *Myxosporio Juglandis* Allescher (Ber. Bayer. bot. Ges. V (1897) p. 21 et Sacc. Syll. XIV, 1015) conidiis biocellatis, minoribus (8—10×2—2$^1/_3$ μ contra 10—14×3$^1/_2$—4$^1/_2$ μ) et basidiorum bene evolutorum praesentia (Pl. IV, fig. 14).

β. *Scoleco-Allantosporae.*

CRYPTOSPORIUM Kunze.

87. Cryptosporium Siphonis Oud. n. sp. — On branches of *Aristolochia Sipho*. — Nunspeet, April 12, 1898; Mr. Beins.

Pustulae numerosae, inaequaliter distributae, parum prominentes, sub peridermatis portiunculo nigrefacto, postremo centro perforato,

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occultatae, 1/5 mill. in diam. Conidia hyalina, bacillaria, ad polos rotundata, continua, 10—20×1/3 μ.

LIBERTELLA Desmazières.

88. LIBERTELLA AUCAPARIAE Oud. n. sp. — On branches of *Sorbus Aucuparia*. — Naaldwijk, Dec. 1866; the late Dr. J. E. VAN DER TRAPPEN.

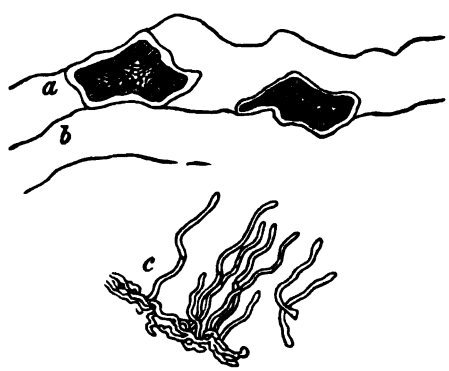
Pustulae valde numerosae, dense aggregatae, peridermate velatae, difformes, saepe confluentes, p.m. inflatae, intus nigrae. Conidia valde subtilia, falcata, 14—16×1 1/6 μ, ad polos acicularia, hyalina, basidiis aequilongis et aequilatis, hyalinis, rectis suffulta.

Differt a *Libertella Ariae* Allescher, Ber. Bayer. bot. Ges. IV (1896) p. 37 et Saccardo Syll. XIV, 1035, pustularum colore neutiquam rubente, conidiorumque longitudine paullo majore (18—25× 1 μ contra 4—16×1 1/6 μ).

89. LIBERTELLA OPULI Oud. n. sp. — On the young branches of *Viburnum Opulus*. — Nunspeet, April 3, 1899.

Acervuli sparsi, peridermate velati, paullo inflati, aurantiaci, elliptici vel oblongi, 1/2—1 1/2×1/2—3/4 mill. Conidia cylindrica, botuliformia, ad polos rotundata, continua, singula hyalina, aggregata pallide aurantiaca, basidiis aequilongis suffulta.

Fig. 5.



Libertella Syringae Oud.
a. cork-layer.
b. bark.
c. basidia and conidia.

90. LIBERTELLA SYRINGAE Oud. n. sp. — On branches of *Syringa vulgaris*. — Bussum, July 1900; Mr. C. J. KONING.

Acervuli numerosi, quoad formam et dimensiones maxime variabiles, nigri, saepe confluentes, nunc poro, tunc vero rima dehiscentes, lateque aperti. Conidia cavernulas septis spuriis radiantibus varie divisas, periderma inter et parenchyma corticale collocatas, implentia, filiformia, curvata vel flexuosa, hyalina, utrimque rotundata, eguttulata, 20—24×1.4 μ. Basidia acicularia, 10—12 ×1.5 μ, e strato proligero fuligineo oriunda, post conidiorum lapsum hamato-curvata.

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*Libertella Ulmi suberosi Oud. n. sp. N. K. A. 3, I, 507 et Hedw. XXXVII, 180. — On branches of *Ulmus suberosa*. — Scheveningen, Dec. 1894.

γ. Phaeosporae.

MELANCONIUM Link.

*Melanconium Persicae Oud. n. sp. N. K. A. 3, I, 508 et Hedw. XXXVII, 180. — On the youngest internodes of *Persica vulgaris*. — the Hague, April 1889.

δ. Didymosporae.

MARSONIA Fischer.

*Marsonia Secales Oud. n. sp. N. K. A. 3, I, 509 et Hedw. XXXVII, 181. — On the leaves of *Secale cereale*. — Winschoten, June 1897. — Sent by Prof. Ritzema Bos.

SEPTOMYXA Saccardo.

91. Septomyxa Ariae Oud. n. sp. On the branches of *Sorbus Aria*. — Scheveningen 1894.

Pustulae numerosae, dense aggregatae, peridermate velatae, eoque rupto hiantes et globulum conidiorum fuliginosum exponentes. Conidia fusiformia, ad polos rotundata, bilocularia, non constricta, hyalina, 8—11×2—2$^1/_3$ μ, basidiis brevibus suffulta.

92. Septomyxa Corni Oud. n.sp. — On the branches of *Cornus alba*. — Nunspeet, March 5, 1899; Mr. Beins.

Pustulae valde prominentes, orbiculares vel ellipticae, irregulariter dispersae, longitudinem 2, latitudinem 1 mill. attingentes, primo peridermate velatae, postremo, peridermate secundum longitudinem fisso, fissuraque usque ad circuitum dilatata, hiantes, conidiorumque glebulam griseam, humectatam caseosam, in parenchymate corticali immersam, exponentes. Conidia sinuose ordinata, fusiformia, hyalina, bilocularia, ad polos anguste rotundata, 14—19×2$^1/_2$ μ.

*Septomyxa Negundinis Oud. n. sp. — Cf. N. K. A. 3, I, 510;

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Hedw. XXXVII (1898) p. 180. — On the branches and petioles of *Negundo fraxinifolia*. — Apeldoorn, Aug. 1896; O.

ε. *Phragmosporae.*

CORYNEUM Nees.

CORYNEUM POPULI Oud. n. sp. — Cf. N. K. A. 3, I, 510; Hedw. XXXVII (1898) p. 181. — On branches of Poplars. — Scheveningen, Oct. 1894.

SEPTOGLOEUM Sacc.

93. SEPTOGLOEUM CORNI Oud. n. sp. — On branches of *Cornus sanguinea*. — Naaldwijk, April 1867; the late Dr. J. E. VAN DER TRAPPEN. — On branches of *Cornus alba*. — Nunspeet, March 8, 1899; Mr. BEINS.

Pustulae valde numerosae, dense congestae, 1/4 mill. in diam., paullo prominentes, primo peridermate velatae, postremo perforatae, in cortice immersae. Conidia solito robustiora, 40—50 × 2 1/3 μ, cylindrica, curvula vel flexuosa, pluriseptata, ad polos rotundata, hyalina. Cirrhi albi.

† † † MUCEDINEAE.

α. *Amerosporae.*

OOSPORA Wallroth.

*OOSPORA ABIETUM Oud. n. sp. — Zittingsversl. Kon. Akad. v. Wetensch. Januari 1897; N. K. A. 3, I, 511; Hedw. XXXVII (1898) p. 181. — On the leaves of *Abies excelsa* and other species of this genus. — Apeldoorn and Laren, Oct. 1896. — O. and Prof. RITZEMA BOS.

SPOROTRICHUM Link.

94. SPOROTRICHUM HELLEBORI Oud. n. sp. — On dying leaves of *Helleborus foetidus*. — Hortus bot. at Amsterdam, Febr. 1890. — Oud.

Maculae amphigenae, valde extensae, fuligineae, fertiles in utraque

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pagina. Conidiorum conglomerationes orbiculares, albae, $^1/_2$ cent. in diam. Hyphae substrato applicatae, valde ramosae, laxe intertextae, septatae, ramulis ultimis subtilissimis. Conidia solitaria, fusiformia, continua, hyalina, ad polos acuta, 3—3.5 $\times$ 2 μ.

MONOSPORIUM Bonorden.

*MONOSPORIUM GALANTHI Oud. n. sp. — Zittingsversl. Kon. Acad. v. Wetensch. 21 April 1897; N. K. A. 3, I, 514; Hedw. XXXVII (1898) p. 181. — On rotting bulbs of *Galanthus nivalis*; Tessel, Febr. 1897; Prof. RITZEMA BOS.

BOTRYTIS Micheli et Link.

*BOTRYTIS PAEONIAE Oud. n. sp. — Zittingsversl. Kon. Akad. v. Wetensch. 21 April 1897; N. K. A. 3, I, 516; Hedw. XXXVII (1898) p. 182. — On young sprouts of a cultivated *Paeonia*. — Rijswijk, April 14, 1897.

OVULARIA Saccardo.

*OVULARIA RANUNCULI Oud. n. sp. — N. K. A. 3, I, 521; Hedw. XXXVII (1898) p. 182. — On the leaves of *Ranunculus acer*. — Apeldoorn, Sept. 1897; O.

β. Didymosporae.

HORMIACTIS Preuss.

*HORMIACTIS HEMISPHAERICA Oud. n. sp. — N. K. A. 3, I, 521; Hedw. XXXVII (1898) p. 182. — On the weakened anthers of *Iris Pseudacorus*. — Leiden, June 1894; Mr. L. VUYCK.

γ. Phragmosporae.

FUSOMA Corda.

*FUSOMA GALANTHI Oud. n. sp. — Zittingsversl. Kon. Akad. v. Wetensch. 21 April 1897; N. K. A. 3, I, 522; Tessel, Febr. 1897; Prof. RITZEMA BOS.

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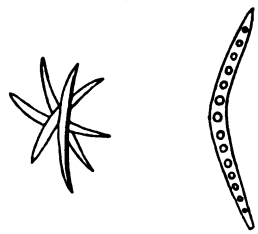
Fig. 6.



Fusoma Heraclei Oud.

95. FUSOMA HERACLEI Oud. n. sp. — On the leaves of *Heracleum Sphondylium*. — Nunspeet, July 8, 1899; Mr. BEINS.

Epiphylla. Maculae sparsae, parvae, saepe autem confluentes et majorem superficiei partem occupantes, niveae vel roseo-variegatae, absque mycelii vestigio. Basidia nulla. Conidia in maculas congesta, varie accumulata, fusiformes, curvata, basi truncata, vertice acuta, primo continua, protoplasmate granuloso repleta, deinde serie longitudinali guttularum ornata, postremo septata (?), 45—60 × 4 μ. Partes dextrorsum et sinistrorsum a curvatura divergentes quoad longitudinem dissimiles.

SEPTOCYLINDRIUM Bonorden.

*SEPTOCYLINDRIUM MORCHELLAE Oud. n. sp. — N. K. A. 3, I, 522; Hedw. XXXVII (1898) p. 183. — On putrified *Morchella esculenta*, Leiden, April 24, 1894; Mr. L. VUYCK.

96. SEPTOCYLINDRIUM SECALIS Oud. n. sp. — On the leaves of germinating rye-plants (*Secale cereale*). — Diepenheim, March 30, 1899. — Sent by Prof. RITZEMA BOS.

Maculae pallescentes in parte dimidia anteriore foliorum viridium vel rubescentium. Hyphae albae, late extensae, hyalinae, ramosae, septatae. Conidia cylindrica, ad polos rotundata, 20—50 × 2½, primo continua, postremo 3- 7- septata. Haec in exemplis junioribus in series simplices vel ramosas ordinata offenduntur.

Fig. 7.

Phymatotrichum baccarum Oud.
Fruit-pulp with fructifying mould-filaments.

97. PHYMATOTRICHUM BACCARUM Oud. n. sp. — In the nearly ripe fruits of *Ribes Grossularia*. — Wormerveer, July 1900. — Sent by Prof. Dr. J. RITZEMA BOS and Mr. C. J. J. VAN HALL.

This Mucedinea begins and closes its life in the fruit-flesh of the just now mentioned shrub, and thus forms an exception to the common rule for all Mucedineae that the conidia-bearing hyphae do not fructify before the moment they have come beyond

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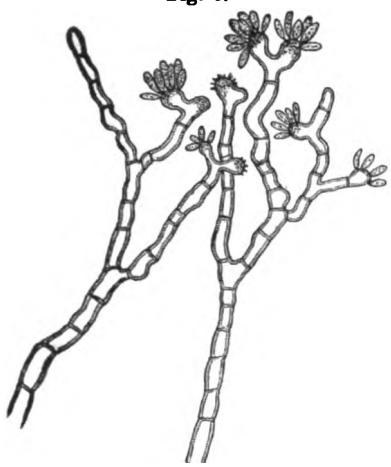
Fig. 8.

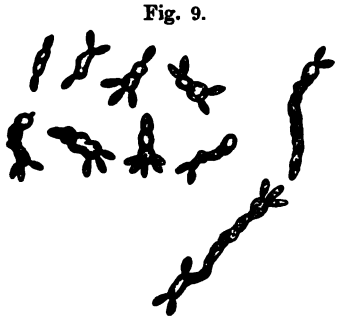


Idem. Fructifying mould-filaments separately.

the surrounding in which their mycelium filaments developed.

The greenish but not quite ripe berries, manifest their less favorable condition by the forming of light ocre-yellow spots, mostly close to the insertion of the fruit-stalk, by which the supposition gets some probability that the point of attack of the fungus is at the base, and not at the summit of the fruit, notwithstanding the latter, by the presence of a little hole at that place, surrounded by the remnants of the calix, might justify the idea that this would be the very place to cause the conidia of an earlier generation to germinate.

Fig. 9.



Idem. Germinating conidia.

The yellow spots soon become brown and seem by preference to follow the course of the nerves or vascular bundles; still it is not well possible to state whether the surrounding parenchyma would be spared by the fungus.

The expectation that the hyphae hidden in the fruit-flesh, shortly after the affected fruits had been removed under favorable conditions to a glass-bell, would produce fertile little cushions at the surface, was by no means realised. There appeared indeed slits which gave the sap within an opportunity to come out in drops charged with independent conidia, but instead of the expected cushions there appeared nothing else but very common moulds and these soon took hold of the greater part of the surface of the berries.

Fig. 10.

Conidia separately.

This result induced Mr. VAN HALL to set in a renewed examination of the hyphae hidden in the fruit, whence arose the certainty that the conidia were exclusively produced within the fruits, between the parenchyma-cells and remained confined in the epidermis of the berries.

The hyphae which amid the fruit-pulp cross in all directions, have a sinuous course and are, by rather closely succeeding partitions, divided into cells of various sizes. Mostly they are in the middle or thereabout a little swollen. The lower branches, springing from

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the main hyphae, appear at different heights and resemble the former, with this difference however, that they degrade in width. Higher up they become shorter and bifurcate so as to form branchlets which are either both fertile or sterile, or one fertile and the other sterile. In the latter case the sterile branch is now straight, now crooked, and besides, mostly surpasses the fertile one in length. The fertile branches always end in a vesicle-shaped cell charged with the task of forming the conidia. The latter repose on short basidia whose number varies from 3—10. They are oblong, colourless, 7—12 × $2^1/_3$—5 μ, and undivided. When ripe they let go hold of the basidia, which then remain sticking as little pricks to the vesicles.

The conidia can be very well cultivated in a moist chamber. After a short time Mr. VAN HALL saw them germinate, i.e. either without the intervenience of a mycelium form new conidia; or at one extremity produce secondary conidia and at the other a sterile mycelium; lastly, also: at one pole form secondary conidia, and at the other push forward a fertile mycelium, of which the top-cell swells up into a vesicle, which gives birth to a certain number of tertiary conidia reposing on short basidia. It may be conceived that in this way the number of conidia must so prodigiously increase that the exuding drops can be partly filled with them. The mother-spore always remains recognisable by its 1 or 2 large vacuoles.

Diagnosis: Caespitibus nullis, sed hyphis in ipsis baccarum parenchymate succulento fructificantibus, intricatis, hyalinis, valde flexuosis, septatis, ex articulis utplurimum curtis, saepe p.m. torulosis, compositis; infra vage ramosis, sursum semel vel pluries bifurcatis; ramis ultimis nunc ambobus, tunc alterutro sterilibus; ramis fertilibus apice globuloso-inflatis, muriculato-conidiophoris; sterilibus apicem versus angustioribus, obtusis, rectis vel curvatis. Conidiis oblongis, utrimque obtusis, hyalinis, continuis, 7—12 × $2^1/_3$—5 μ, protoplasmate denso, guttulisque 1 ad 2 voluminosis repletis. Articulis hypharum 7—10 μ crassis.

† † † † DEMATIEAE.

α. Didymosporae.

FUSICLADIUM Bonorden.

98. FUSICLADIUM CARPOPHILUM Oud.; Cladosporium carpophilum Thüm. Oest. bot. Zeits. 1877, p. 12; Thüm. Wiener Landwirthsch.

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Wochenblatt 1877. p. 480; Thüm. Fgi pomicoli 1855, p. 13; Sacc. Syll. IV, 353. — On the young fallen fruits of *Persica vulgaris*, in company of *Monilia fructigena*. Raamsdonk, June 25, 1898. — Sent by Prof. J. RITZEMA BOS.

Maculae orbiculares, $^1/_2$ cent in diam., primo sub epidermidis lanugine occultatae et imperceptibiles, postea vero, colore magis saturato fucatae, facilius distinguendae. Observantur in iis hyphae erectae, curtae, rectae vel flexuosae, fuscescentes, 1—3-septatae, ex mycelio superficiali repente sursum tendentes. Conidia acrogena, ovoidea vel fusiformia, vulgo continua, rarius bilocularia, conidiophoris pallidiora, 20×5—6 μ.

*FUSICLADIUM FAGOPYRI Oud. n. sp. Zittingsversl. Kon. Akad. v. Wet. 26 Juni 1879; Ned. Kr. Arch. 3, I, 524; Hedw. XXXVII (1898) p. 183. — On leaves of *Fagopyrum esculentum*. — Goor, June 26, 1837; sent by Prof. J. RITZEMA BOS.

In Hedwigia Pisum sativum was also mentioned as the foster-plant. This name should however be blotted out.

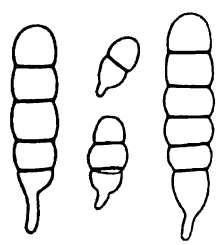
β. Phragmosporae.

CLASTEROSPORIUM Schweinitz.

*CLASTEROSPORIUM IRIDIS Oud. n. sp. — Hedw. XXXVII (1898) p. 318. — On the leaves of *Iris xyphoides*, by gardeners mostly called *I. anglica*. — Leiden June 17, 1898. — Sent by Prof. J. RITZEMA BOS. (Pl. IV, fig. 16).

99. CLASTEROSPORIUM LINI Oud. n. sp. — On the roots of *Linum usitatissimum*. — Wageningen, Febr. 1900; sent by Prof. RITZEMA BOS.

Fig. 11.



Clasterosporium Iridis Oud. — Conidia.

Conidia superficialia, solitaria, cylindrica, satis regulariter distributa, a mycelio in telis internis abscondito producta, pallide umbrina, recta vel curvata, ad polos rotundata, versus basin in pedicellum breve (7—10 × 2 — 3 μ), hyalinum, continuum attenuata, vulgo 4-septata, vix constricta. Conidia 4-septata mensuris respondent 35—40 × 10—12 μ compartimentaque ostendunt fere aequalia. Membrana conidiorum ad septorum circuitum profundius tincta.

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CRYTPOCORYNEUM Fuckel.

100. CRYPTOCORYNEUM OBOVATUM Oud. n. sp. — On mouldering wood of *Quercus Robur*. Valkenburg (L.), April 1900; Mr. J. RICK. — Caespituli suborbiculares, $^1/_8$—$^1/_6$ mill. in diam., numerosi, p. m. dense congesti, aterrimi. Conidia late-obovata, 4-septata, fuliginea, fere opaca, ad septa non constricta, 35—46×16$^1/_3$—18$^2/_3$ μ, cellula basilari minima prorsus hyalina aucta.

Cellularum omnium tinctarum — numero 4 — duae supremae in corpus late-ellipticum vel late obovatum conjunctae, maximae, duae infimae contra, cum cellula basilari hyalina in pedunculum brevem quasi colalitae. Septum supremum conidium vesiculiforme proprio dictum in partes 2 valde inaequales: superiorem nempe minorem, inferiorem contra majorem dividit (Pl. IV, fig. 15).

HELMINTHOSPORIUM Link.

101. HELMINTHOSPORIUM GRAMINEUM Rabh. et Oud. — Cf. Zittingsv. Kon. Ak. v. Wet. 26 Juni 1897; Hedw. XXXVII (1898), p. 183. — Synonymous with *H. teres* Sacc. Fgi ital. del. tab. 833 and Syll. IV, 412, and with *H. gramineum* Eriksson „Ueber eine Blattfleckenkrankheit der Gerste" a^0. 1885, taken over as an extract Botan. Centralblatt XXIX, 1887, p. 83 and in Frank, „Die Krankheiten der Pflanzen" 2^e Ed. p. 316 (a^0. 1895). — Rabenhorst's fungus, published in 1857, in his Herb. mycologicum Ed. 2^a n^0. 332, does not differ from the two other mentioned and, accordingly, the name given by him must be preserved by right of priority.

BRACHYSPORIUM Saccardo.

*BRACHYSPORIUM PISI Oud. n. sp. — Cf. N. K. A. 3, I, 527; Hedw. XXXVII (1898) p. 183. — On the leaves of *Pisum sativum*; Warfum, June 17, 1897. Sent by Prof. J. RITZEMA BOS.

CERCOSPORA Fresenius.

102. CERCOSPORA SPINACEAE Oud. n. sp. — On the leaves of *Spinacea oleracea*. — Nunspeet, June 9, 1899. — Mr. BEINS.

Maculae amphigenae, utrimque fertiles, pallide viridescentes vel stramineae, variae extensionis (1—10 mill.), saepe confluentes; hyphae simplices, fere bacilliformes, continuae vel versus apicem 1-septatae,

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fuligineae, ad polos rotundatae, 40—70×3½ μ. Conidia acrogena, primo elliptica, denique oblonga vel bacillaria, nodosa; postremo cylindraceo-fusiformia, curvata, ad polos rotundata vel acuta, medio septata, hyalina, 16—20×3 μ.

Differt a *C. dubia* Wint. conidiis multo brevioribus et angustioribus (16—20×3 μ contra 60—70×8—9 μ) et a *C. beticola* conidiis multo brevioribus (16—20 contra 70—120 μ) et 1- neque dense septulatis.

HETEROSPORIUM Klotzsch.

103. HETEROSPORIUM ALLII Ellis et Martin, Journ. of Mycol I, 100, var *Polygonati* Oud. n. v. — On the leaves of *Polygonatum multiflorum.* — Nunspeet, Oct. 2, 1899; Mr. BEINS.

Caespites amphigeni, irregulariter distributi in partibus foliorum polymorphis, satis extensis, zona purpurascente variae latitudinis circumscripti; hyphae simplices vel ramosae, septatae, p. m. nodosae, 140—190×7 μ, olivaceo-fuliginosae. Conidia acrogena, primo hyalina, ovoidea, continua; denique elliptica vel oblonga, pallide-fuliginea; postremo oblonga, 2- vel 3-septata, subtilissime muriculata, pallide olivacea, 28×11—12 μ, ad septorum altitudinem leviter constricta.

104. HETEROSPORIUM AVENAE Oud. Hedw. XXXVII (1898), p. 318. — On the leaves of *Avena sativa* (Ulrum) and *Hordeum vulgare* (Dordrecht). — Sent by Prof. J. RITZEMA BOS. — Though in a letter to Prof. RITZEMA BOS I changed the above name into *H. Cerealium* (see his account concerning the informations given in 1899, issued from the phytopathological Laboratory WILLIE COMMELIN SCHOLTEN at Amsterdam), because the fungus was found, besides on Oats, later also on Barley, I have still come back to my first denomination by reason of rights of priority.

*HETEROSPORIUM SYRINGAE Oud. n. sp. — N. K. A. 3, I, 529; Hedw. XXXVII (1898), p. 183. — On branches and fruits of *Syringa vulgaris.* Nunspeet, Nov. 1896; Mr. BEINS.

γ. *Dictyosporae.*

CONIOTHECIUM Corda.

*CONIOTHECIUM MUGHI Oud. n. sp. Hedw. XXXVII (1898) p. 318.

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— On the peltate summits of the fruit-scales of *Pinus Mughus*. — Nunspeet, April 11, 1898; Mr. BEINS.

105. CONIOTHECIUM PSAMMAE Oud. n. sp. — On the leaf-sheaths of *Psamma littoralis* (Ammophila arenaria). — Downs near Brielle. Sept. 1871; Oud.

Caespites minimi, punctiformes, in sulcis foliorum longitrorsum seriati, solitarii vel confluentes. Conidia pluricellularia, h.e. in varias directiones divisa, polymorpha, variae dimensionis; cellulae componentes glebularum globulosae vel multangulares, ferrugineae, $4^2/_3$—$7\,\mu$ in diam.

† † † † † STILBEAE.

HYALOSTILBEAE.

Amerosporae.

STILBUM Tode.

106. STILBUM TOMENTOSUM Schrad. Journ. 1799, II, p. 65 et tab. III, fig. 2; Grev. Scott. Cr. Fl. tab. 281; Stilbum parasiticum. Ditmar in Sturm. Cr. Fl. Bd. I, 93 et tab. 46; Sacc. Syll. VII, 566. — Valkenburg (L.) 1899; Mr. J. RICK. — On *Hemiarcyria clavata*, sticking to mosses and liverworts.

Myxomycetis sustentaculum praebentis color naturalis non distinguendus, quippe qui tota planta fungi parasitantis mycelio involvitur. Stilbi exempla omnia e pedunculo et capitulo terminali composita, cum ipso tegumento concolaria. Pedunculus et capitulum a se invicem distincta persistunt. Superficies pedunculi tomentosa ad nomen specificum constituendum a Schradero adhibita est, neque vero fila tenuia quae ex eo assurgunt cum glandulis comparanda, uti passim ab auctoribus factum est. Sistunt enim hyphas periphericas a corpore axili extrinsecus divergentes, singulas conidio minimo terminatas.

Pedunculos longos invenimus $^1/_2$ mill., crassos $35\,\mu$; capitula vero $120\,\mu$ in diam. Conidia perfecte globosa, hyalina, continua, $1^1/_6\,\mu$ in diam. Hyphae pedunculum constituentes filiformes ad capituli basin divergunt, corpusculumque formant globosum, cujus superficies farina quasi obducta, conidia innumera ostentat.

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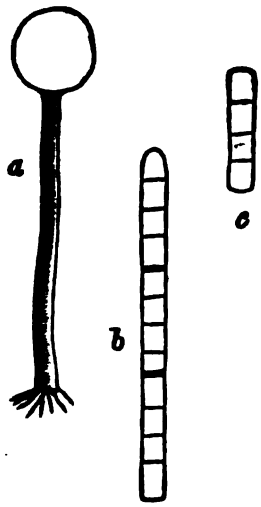
Fig. 12.



Arthrobotryum coprophilum Oud. — *a.* Stalk with capitulum; *b.* 3 chained conidia; *c.* conidium separately.

PHAEOSTILBEAE.

Phragmosporae.

ARTHROBOTRYUM.

107. ARTHROBOTRYUM COPROPHILUM Oud. n. sp. — On horse-turds. Amsterdam, Oct. 1899. — Mr. C. J. J. VAN HALL.

Laxe gregarium. Stipites conidiophori cylindracei, alti $^1/_2$ ad $^3/_4$ mill., lati 60—80 μ, stricti, laeves, glabri, nigri, ex hyphis filiformibus pallide fuscis, septatis formati. Capitula globulosa, lactea, $^1/_6$—$^1/_4$ mill. in diam. Conidia catenulata, cylindrica, hyalina, ad polos truncata, excepto tamen polo anteriore conidii ultimi, omnia 3-septata, 16—28×4—5$^1/_2$ μ.

† † † † † † TUBERCULARIEAE.

TUBERCULARIEAE MUCEDINEAE.

Amerosporae.

HYMENULA Fries.

*HYMENULA PSAMMAE Oud. n. sp. Cf. N. K. A. 3, I, 532; Hedw. XXXVI (1898), p. 184. — On the stems of *Psamma littoralis* (Ammophila arenaria). — Loosduinen, 1894.

Phragmosporae.

FUSARIUM Link.

*FUSARIUM OPULI Oud. n. sp. Cf. Hedw. XXXVII (1898), p. 318. — On branches of *Viburnum Opulus*. — Nunspeet, June 15, 1898; Mr. BEINS.

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TUBERCULARIEAE DEMATIEAE.

Amerosporae.

CHAETOSTROMA Corda.

*CHAETOSTROMA CLIVIAE Oud. n. sp. Zittingsversl. Kon. Akad. v. Wetensch. 28 Nov. 1896, p. 226; Ned. Kr. Arch. 3, I, 533; Hedw. XXXVII (1898), p. 184. — On the leaves of *Clivia nobilis*. — Hees near Nijmegen; October and November 1896. — Prof. RITZEMA BOS.

† † † † † † † MYCELIA STERILIA.

108. ECTOSTROMA TRIGLOCHINIS Oud. n. sp. — On the stems of *Triglochin palustre*. — Nunspeet, Oct. 8, 1899; Mr. BEINS.

Maculae nigrae, juxta longitudinem ad superficiem caulium extensae, structurae parenchymaticae, e seriebus cellularum partim longiorum, partim breviorum, nunc alternatim tunc vero absque ordine dispositarum, semper vero arctissime inter se cohaerentium, stomatibus exceptis sine meatuum intercellularium vestigio contextae. Maculae, vel potius membranae longitudinem attingunt 3 centim. internodiaque vel caulem perfecte involvunt. Sporulae non visae.

Chemistry. — Prof. C. A. LOBRY DE BRUYN presents, also on behalf of Mr. W. ALBERDA VAN EKENSTEIN a paper entitled: "*A new kind of formal-(methylene-)compounds of some oxy-acids.*"

In the preparation of the formal-compounds of polyhydric alcohols and of oxy-acids it has been necessary up to now to call in the aid of a strong mineral acid to effect the condensation. The change which then occurs takes place between the formaldehyde and the hydroxyl groups which possess an alcohol function; in the case of the oxy-acids the carboxyl groups take no part in the reaction so that the formed compounds still remain acids.

In the case of several oxy-acids, namely those which contain in their molecule only one alcoholic hydroxyl group, the efforts to prepare

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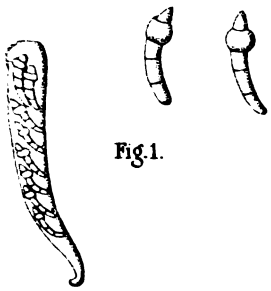

Fig.1.

Fig.2.

Fig.3.

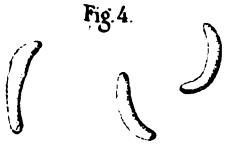

Fig.4.

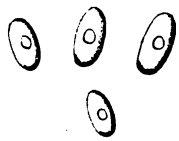

Fig.5.

Fig.6.

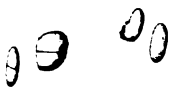

Fig. 7.

Fig.8.

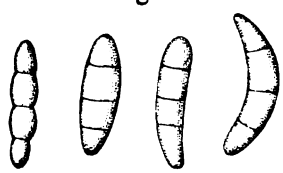

Fig.9.

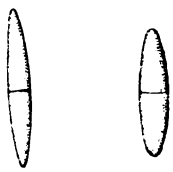

Fig. 10.

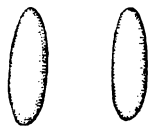

Fig.11.

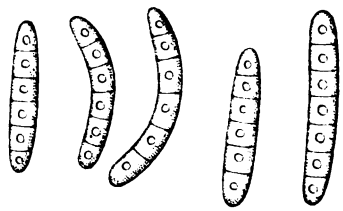

Fig.12.

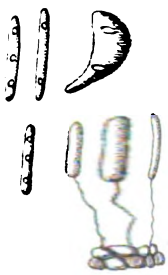

Fig.13.

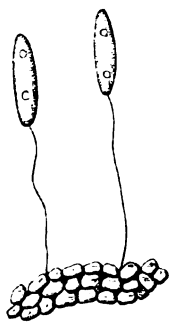

Fig.14.

Fig.15.

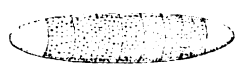

Fig.16.

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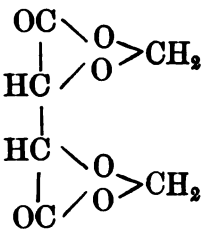
formal-compounds have only given a negative result. Even with tartaric acid which contains two hydroxyl groups, WEBER and TOLLENS [1]) only succeeded with difficulty in getting a very small quantity of a compound of which they are still in doubt whether it may be really derived from the unaltered acid.

We have found some time ago that formaldehyde reacts with tartaric, citric, malic and lactic acids when operating in purely aqueous solutions. The compounds found happen to be extraordinarely sensitive towards acids; these at once restore the components. The new formal-compounds also differ from those already known because, at their formation, the carboxyl group takes part in the reaction. In the case of tartaric acid a compound is formed which no longer possesses acid properties; the tribasic citric acid becomes dibasic and the dibasic malic acid becomes monobasic.

The new compounds are formed by repeated evaporation of the solution of the acids with an excess of formaldehyde. As the acid itself prevents its reaction with formaldehyde and the compound already undergoes a slight decomposition in the presence of warm water, it is not astonishing that each time only a small quantity (about 5 per cent) is formed which must be extracted by shaking with ether or better still with chloroform or benzene. Sometimes the compound crystallises slowly from the concentrated syrup. When removed by shaking out, the residue may be again treated with formaldehyde in order to obtain a fresh quantity. We are, therefore, dealing here with an equilibrium.

From d-tartaric acid was obtained a white substance crystallising in needles with a melting point of 117° and a rotatory power of + 112°. According to the analysis and the determination of the number of methylene groups by means of phloroglucinol and hydrochloric acid, the compound is $C_6H_6O_6$, or:



It is neutral. The composition was also determined by warming with a known quantity of normal alkali and titrating the excess. On evaporating the substance with pure water, or very soon by acids or alkalis, the components are reformed. In quite a similar manner is formed from anti-

[1]) Ann. d. Chem. 299. 335.

[2]) Attempts will be made to determine the mol. weights of this and the following substances.

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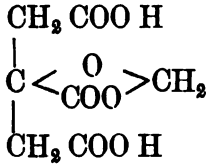
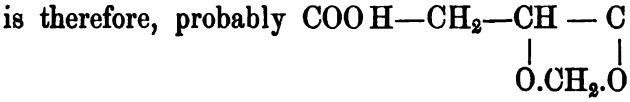
tartaric acid a compound melting at 106° which, as might be expected, is inactive.

It seems very peculiar that we have not succeeded in preparing a formal-compound from uvic acid. This again crystallises unaltered on evaporation even after heating above 100°. It, therefore, seems that the tendency of *d*- and *l*-tartaric acid to unite in concentrated solutions to molecules of uvic acid is greater than that which causes the formation of the very unstable formal-compounds. We will investigate this point more closely as soon as we have the formal-compound of *l*-tartaric acid at our disposal.

Citric acid yields a readily crystallisable compound melting at 200°, which contains only one methylene group. From the analysis and the determination of the formal follows the composition $C_7H_8O_7$; the most probable formula being:



This substance may be first titrated as a dibasic but after warming as a tribasic acid. Malic acid also reacts with formaldehyde; this is already apparent from the change in the rotation. By shaking with benzene an oily liquid may be isolated from the syrupy reaction-product which still remains liquid when strongly cooled. It is nearly insoluble in water, has an acid reaction and is laevorotatory. According to a determination with the aid of phloroglucinol and hydrochloric acid it contains one methylene group. The formula is therefore, probably



With salicylic and oxalic acids no change occurs when they are treated with formaldehyde in the manner described. Other oxy-acids, of which it is already known that they yield formal-compounds by treatment with formaldehyde in the presence of an acid, will be more closely investigated.

It may be further observed that sugars also react with formaldehyde in the absence of an acid. This is shown by the very important changes which take place in the rotations; that of glucose is nearly doubled whilst those of galactose, fructose, arabinose and mannose are considerably lessened; rhamnose which is dextrorotatory becomes laevorotatory. The new compounds are, however, of a syrupy nature; attempts to obtain from them crystallisable substances have therefore not yet been successful. On evaporating them a few times

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with pure water, the combined formaldehyde is volatilised and the unchanged sugars crystallise; the combination is consequently a very feeble one [1]).

The investigation is being continued.

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[1]) We observe that benzaldehyde also reacts when heated with aqueous solutions of tartaric acid, anti-tartaric acid, citric acid and glucose; the products are however, all liquid, syrupy and very unstable. Tartaric acid becomes left-handed and the rotation of glucose is much diminished.

(December 19, 1900).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday December 29, 1900.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 29 December 1900 Dl. IX).

CONTENTS: Dr. J. F. VAN BEMMELEN: "Third note concerning certain details of the Monotreme-skull" (Communicated by Prof. A. A. W. HUBRECHT), p. 405. — Dr. E. VAN EVERDINGEN JR: "On the HALL-effect and the resistance of crystals of bismuth within and without the magnetic field" (continued) (Communicated by Prof. H. KAMERLINGH ONNES), p. 407 (With one plate) — J. C. SCHALKWIJK: "Precise Isothermals". I. (Communicated by Prof. H. KAMERLINGH ONNES), p. 421 (With one plate). — Prof. H. A. LORENTZ: "The theory of radiation and the second law of Thermodynamics", p. 436. — Dr. P. VAN ROMBURGH: "On the essential oil from the leaves of Alpinia malaccensis Rosc." p. 451. — Dr. P. VAN ROMBURGH: "On the action of nitric acid on the esters of methyl-phenylaminoformic acid", p. 451. — Dr. P. VAN ROMBURGH: "On the essential oil from Ocimum Basilicum L.", p. 454.

The following papers were read:

Zoology. — "*Third note concerning certain details of the Monotreme-skull.*" By Dr. J. F. VAN BEMMELEN The Hague. (Communicated by Prof. A. A. W. HUBRECHT.)

Ethmoïd and Maxillo-turbinale.

In the structure of their ethmoïd-bone Ornithorhynchus and Echidna present great differences: the former having only one single opening for the olfactory nerve and furthermore differing from all other mammals by the exceptionally low number of only three ethmo-turbinals; the latter on the contrary showing a lamina cribrosa of uncommon size, while by the very high number of eight primary and a number of secondary ethmo-turbinals it occupies an equally exceptional but opposite position.

Comparing the two Monotremes among themselves, the conclusion

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seems to be justified that the structure of the ethmoïd in Echidna may have developed from a starting point like that of Ornithorynchus by the conchae increasing in number, and thereby necessitating the higher differentiation of the lamina cribrosa.

The question then arises: where have these new conchae made their appearance: before or behind the primary three? The answer must be in the latter sense, as there is no space left at the anterior side of the primary conchae for the intercalation of new ones, because in both animals the naso-turbinal and maxillo-turbinal are placed immediately in front of the first ethmoïdal concha in an absolutely identical position.

I am strengthened in this view by the observation, that in both forms the foramen sphenopalatinum is situated just beneath the third concha: thus, while in Ornithorhynchus it is found at the back side of the conchal area, in Echidna it occupies the interspace under the third and fourth concha.

This opinion harmonizes with the conclusion, which SEYDEL [1]) has arrived at by investigating the development of the nasal area in Echidna. He found the first rudiment of the ethmo-turbinals as one single protuberance on the lateral wall of the nasal cavity, which afterwards became divided into three parts by vertical grooves. SEYDEL makes reference to the observations of W. N. PARKER [2]), on a young of Echidna, which showed six ethmo-turbinals, decreasing in size from before backwards, and thereupon gives as his opinion: (p. 515): "This gives certain evidence of a successive formation of new (olfactory) knobs behind the first-formed."

In most mammals the increase in number of the conchae in a caudal direction goes hand in hand with the excavation of the body of the sphenoïd bone, i. e. the development of the sinus sphenoïdalis, by means of which the necessary space is obtained for the lodging of the new conchae. Echidna is among these mammals, for at the bottom of the hindmost five conchae a horizontal bony plate is to be found, taking its origin from the underside of the floor of the sella turcica, and stretching forward towards the level of the foramen sphenopalatinum, where it ends in a sharp concave border.

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[1]) SEYDEL. O. Ueber Entwicklungsvorgänge an der Nasenhöhle und am Mundhöhlendache von Echidna nebst Beiträgen zur Morphologie des peripheren Geruchsorgans und des Gaumens der Wirbelthiere, in R. SEMON, Zoologische Forschungsreisen in Australien und dem Malayischen Archipel. Bd. III Lief. 3.

[2]) PARKER. W. N. On some points in the structure of the young of Echidna aculeata. Proc. Zool. Soc. London 1894.

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In other mammals this bottom-plate of the sphenoïdal sinus has been called by SEYDEL lamina terminalis or "untere Schlussplatte."

Though in Echidna it is well developed and easily visible in a paraseptal section through the macerated skull, its occurrence in this animal hitherto seems to have escaped notice, for not only is it absent in the figure ZUCKERKANDL has given in 1887 in his „Geruchsorgan der Säugethiere", but it is equally omitted in the more recent illustration of GEGENBAUR's new Handbook of Vertebrate comparative anatomy (1898).

The structure of the maxillo-turbinal is the same in both Monotremes; it corresponds to the „verästigte" (ramified) type of HARWOOD-WIEDEMANN, the only difference between the two forms being that in Ornithorhynchus it is somewhat larger and more complicated.

ZUCKERKANDL's statement, that there exists a difference in this respect between Echidna and Ornithorhynchus, the first having a doubly-coiled („doppeltgewundenes"), the latter a folded („gefaltenes") maxillo-turbinal is erroneous, and it is all the more desirable that this mistake should be elucidated, as it has found its way unaltered into GEGENBAUR's new handbook. Yet, as far as regards Ornithorhynchus, the veracity of the statement had already been challenged by SYMINGTON [1]), and for Echidna, by W. N. PARKER (l.c.) who, though agreeing with SYMINGTON, yet came to the conclusion, that Echidna's „maxillary turbinal apparently belongs to the folded („gefaltene") and not to the doubly-coiled („doppeltgewundene") variety."

Transverse sections through the organ, in the preserved as well as in the macerated state, leave no doubt that there exists a complete agreement between Ornithorhynchus and Echidna, both showing a well-marked branching type.

Physics. — Dr. E. VAN EVERDINGEN JR., "*On the* HALL-*effect and the resistance of crystals of bismuth within and without the magnetic field*" (Communication N°. 61 (continued) from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

4. *Complete results for the* HALL-*coefficient.* It was mentioned in § 2 of the first part of this Communication [2]) that the relation

[1]) SYMINGTON, J. On the nose, the organ of Jacobson and the dumb-bell-shaped-bone in the Ornithorhynchus. Proc. Zool. Soc. London 1891, pag. 575.

[2]) Versl. d. Verg. Kon. Ak. v. Wet. 29 Sept. 1900, p. 277. Comm. Phys. Lab. Leiden, N°. 61.

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found before between the HALL-coefficient and the position of the principal axis with respect to the lines of magnetic force was confirmed in these recent experiments. The bar N°. 1, with its longest dimension parallel to the principal axis, and N°. 2, 3 and 5, with their longest dimension and two sides perpendicular to the principal axis (for the position of these bars compare fig. 1 in the first part of this paper) were each tested in four positions. In these the longest dimension (also direction of current) was always horizontal and perpendicular to the lines of force of the horizontal electromagnet, while each of the four sides consecutively took the upper horizontal position. Hence with N°. 1 the principal axis was always perpendicular to the lines of force (position ⊥), with 2, 3 and 5 alternately perpendicular to and parallel to the lines of force (position //). For the sake of simplicity the differences between the results in the four positions of N°. 1 and in the two positions ⊥ or // of the other bars will not be mentioned, and only mean values will be given. Very likely these differences are caused by small irregularities in crystallisation and small deviations from the exact position in the experiments, and they are not to be compared to the differences between positions // and ⊥.

All observations have been reduced to the same magnetic fields [1]) and to the same temperature (15° C.).

HALL-coefficient R.

N°.	Magnetic field.			
	4600		2600	
	⊥	//	⊥	//
1	— 8.0	—	—10.2	—
2	—10.6	—0.2	—12.6	—0.7
3	— 8.8	0.0	—11.1	—0.4
5	— 8.2	+0.6	—10.6	—0.1

The small value of the coefficient in the position // and the reversal of sign with N°. 5 were first pointed out in § 2 of the first part of this paper.

---

[1]) The numbers given in § 2 for the magnetic field appeared afterwards a little too high. For this reason and on account of the correction for temperature the numbers for 2, 3 and 5 differ slightly from those given before.

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From the numbers in the columns headed ⊥ it appears that the experiments afford no reason for making a distinction between the positions in which the *current* is parallel (as with 1) and those in which the *current* is perpendicular to the principal axis (as with 2, 3 and 5). This seems to indicate that, as was admitted before, only the angle between the principal axis and the lines of force determines the value of the HALL-coefficient.

In order to find the form of this relation the bars N°. 4 and 6, in which the principal axis makes an angle of 60° with two of the sides and is parallel to the other sides, were also tested in two positions.

In isotropic substances the HALL-effect for currents in an arbitrary plane V is determined by the product of "the" HALL-coefficient into the component of the magnetic force perpendicular to that plane. This may however also be regarded as the product of the whole magnetic force into a specific HALL-*coefficient for the plane V*. This coefficient would be obtained by multiplying the coefficient for a normal magnetic force by the cosine of the angle between the actual direction of magnetic force and the normal to the plane V. We shall apply this principle to the HALL-effect in a crystal of bismuth, and for this purpose resolve the magnetic force into the direction of the principal axis and the transverse direction. Let us assume that we found for currents in a plane ⊥ to the principal axis and the magnetic force a HALL-coefficient R_1, for currents in a plane // to the principal axis and ⊥ to the magnetic force a coefficient R_2. The simplest supposition in the case of a magnetic force M in a direction inclined at an angle α to the principal axis is then, that the HALL-effect in the plane ⊥ to M now consists of two parts, one caused by the component $M \cos \alpha$, // to the principal axis, one caused by the component $M \sin \alpha$, ⊥ to the principal axis. The HALL-coefficient R in this case is then given by

$$R = R_1 \cos^2 \alpha + R_2 \sin^2 \alpha.$$

In this deduction for simplicity R_1 and R_2 are taken as constants and not as functions of the magnetic force, as is the case with bismuth. As we aim only at an approximation this will not be open to objection; we remark only by the way that with an isotropic substance where R was a function of M, this method might lead to wrong results.

As appears from the table the value of R_1 for crystalline bismuth is very small as compared with R_2, so that we may omit the

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term with R_1 (which moreover is rather uncertain) except for very small values of α. Then R becomes equal to $R_2 \sin^2 \alpha$.

We give here the values, observed with the bars N°. 4 and 6 in a magnetic field 4600 for R_2 and R_1 and the calculated values $R_2 \sin^2 \alpha$, where α is 30°.

N°.	R_2	R	$R_2 \sin^2 \alpha$
4	10.3	2.5	2.6
6	12.2	3.1	3.1

The agreement between the observed and calculated R is as good as one could wish, so that the simple supposition leading to the formula for R is confirmed. The values for R_2 do not differ too much from those found with the bars 1, 2, 3 and 5.

If the equation for R is written in the following form:

$$1 = \frac{\left(\frac{1}{\sqrt{R}}\right)^2 \cos^2 \alpha}{\left(\frac{1}{\sqrt{R_1}}\right)^2} + \frac{\left(\frac{1}{\sqrt{R}}\right)^2 \sin^2 \alpha}{\left(\frac{1}{\sqrt{R_2}}\right)^2}$$

it appears that R may be obtained by the construction of an ellipsoid of revolution with $\sqrt{R_1}$ as axis of revolution parallel to the principal axis, and $\sqrt{R_2}$ as perpendicular axis. The radius vector in the direction of the magnetic force gives the value of $\frac{1}{\sqrt{R}}$ for the plane perpendicular to the magnetic force.

Also with a view to the results, mentioned below, obtained for the resistance in the magnetic field it appeared useless to connect the HALL-coefficient with the magnetisation (MAXWELL's vector $\mathfrak{B}$), as has been done before [1]).

5. *Resistance of the bismuth crystals.*

The first object of these measurements was to test whether in regularly crystallised bismuth an increase of resistance would occur when the current flows in the direction of the lines of magnetic force. For irregular (cast) bismuth-plates this question had been

[1]) Versl. der Verg. 21 April 1897, p. 501; 26 Juni 1897, p. 69. Comm. N°. 37 p. 18; Comm. N°. 40, p. 3.

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answered in the affirmative by the experiments of GOLDHAMMER [1]) and others. The result of the investigation with three bars of bismuth from MERCK and mentioned in Communication N°. 37, likewise gave an answer in the affirmative. The increase of resistance, though small, was comparable to that found in positions // when the current was perpendicular to the lines of force.

It was now considered desirable to carry out a set of measurements so complete that for an arbitrary relative position of principal axis and magnetic force the resistance in any direction would be known. The bar of which the greatest dimension was parallel to the principal axis, MERCK N°. 3, was however hardly longer than the distance between the "resistance-electrodes", so that for this research other material was required. I found this in the crystal of bismuth put at my disposal by Mr. PERROT and shall now publish only the results obtained with that.

In these experiments we must take into account the relative positions of three directions: principal axis, magnetic force and current. In the figures 2*a*, *b* and *c* (Pl. I) the principal axis is always represented by a single arrow, the magnetic force by a double arrow, while the direction of the current, always coinciding with the longest dimension of the bars, is indicated by radii vectores *Oa*, *Ob*, *Oc* etc.

The experiments in the magnetic field may be divided into three groups:

I. Magnetic force ⊥ to principal axis.
II. „ „ // „ „ „
III. „ „ and „ „ at an angle of 60°.

For group I and II, and for the resistance without magnetic field it was very probable that the resistance in any direction with respect to the principal axis would be found by the aid of an ellipsoid with its axis coinciding with axes of symmetry of the crystal. For, these axes will remain axes of symmetry, so that the relation between electromotive force and current density can be expressed by equations like:

$$X = r_1 u \qquad Y = r_2 v \qquad Z = r_3 w.$$

---

[1]) Wied. Ann. 31, p. 360, 1887.

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When a current I flows in a direction determined by the angles α, β and γ with the axes Oa, Ob and Oc,

$$u = I\cos\alpha, \qquad v = I\cos\beta, \qquad w = I\cos\gamma,$$

while the potential gradient E in the direction (α, β, γ) which measures the resistance, is given by

$$E = X\cos\alpha + Y\cos\beta + Z\cos\gamma$$

hence

$$E = I(r_1\cos^2\alpha + r_2\cos^2\beta + r_3\cos^2\gamma) = rI$$

and

$$r = r_1\cos^2\alpha + r_2\cos^2\beta + r_3\cos^2\gamma \quad . \quad . \quad . \quad . \quad . \quad (*)$$

This written in the form

$$1 = \frac{\left(\frac{1}{\sqrt{r}}\right)^2\cos^2\alpha}{\left(\frac{1}{\sqrt{r_1}}\right)^2} + \frac{\left(\frac{1}{\sqrt{r}}\right)^2\cos^2\beta}{\left(\frac{1}{\sqrt{r_2}}\right)^2} + \frac{\left(\frac{1}{\sqrt{r}}\right)^2\cos^2\gamma}{\left(\frac{1}{\sqrt{r_3}}\right)^2}$$

indicates that r may be found by the construction of an ellipsoid with the square roots of the conductivities in three principal directions as axes.

The measurements indicate, that very likely also the resistances in group III can be found by means of such an ellipsoid.

We will treat now successively of:

1st. the resistances without the magnetic field;

2nd. the resistances along the axes in the three groups in the magnetic field;

3rd. the resistances in other directions, compared with values calculated from the results of 2nd by means of the above formula (*).

6. *The resistances without the magnetic field.*

With each of the six bars the resistance was measured at least four times, i.e. with the resistance electrodes at least once on each of the four sides (after the method described in Communication N°. 48) and mean values were calculated from the results.

The results are given here; r is expressed in the unit 10^{-5} C.G.S., the conductivity λ in the unit 10^{-6} C.G.S., $\sqrt{\lambda}$ in the unit 10^{-3} C.G.S.

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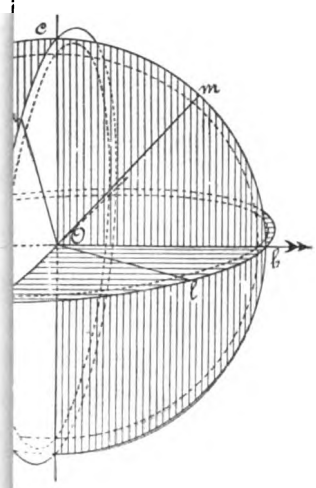
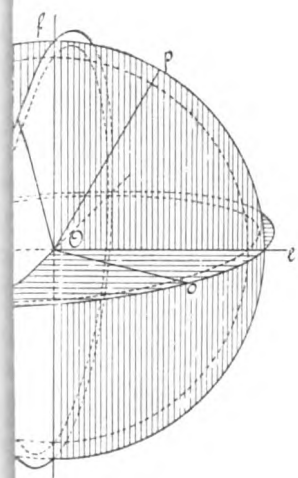
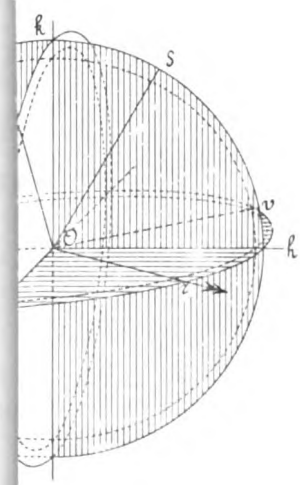
On the HALL-effect and the resistance of without the magnetic field."







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N°.	1	2	3	5	4	6
r	3.48	2.29	2.32	2.07	2 59	2.85
λ	2.87	4.37	4.31	4.83	3.86	3.51
$\sqrt{\lambda}$	1.70	2.09	2.08	2.20	1.96	1.87

It appears that the resistance of N°. 1, that is the resistance in the direction of the principal axis, is considerably larger than that in the transverse directions with 2, 3 and 5. As irregularities in crystallisation can only diminish the ratio of these resistances we are lead to assume that the ratio of the resistances of N°. 1 and 5, 3.48 : 2.07 or 1.68 : 1 approaches nearest to the ratio for a perfect crystal. (Also according to the results for HALL-effect 5 was the most regular bar). For the whole prism PERROT found as ratio of thermo-electric forces $\frac{//}{\perp}$ 2.00 as a mean, hence a ratio of the same order of magnitude.

The mutual differences between 2, 3 and 5 are relatively small. Hence we may assume that these differences would vanish in a perfect crystal, so that the ellipsoid of conduction without the magnetic field would be an ellipsoid of revolution. As axes for this we take the values of $\sqrt{\lambda}$ obtained with 1 and 5, that is 1.70 and 2.20. With these values in the figures 2*a*, 2*b* and 2*c* the lined circles and ellipses have been drawn, all dimensions parallel to the principal axis (←) being reduced in the ratio 2 : 1.

For the direction of N°. 4 and 6 a value of the resistance may now be calculated. We have $\alpha = 60°$, $\beta = 30°$ and $\gamma = 90°$ or $\alpha = 60°$, $\beta = 90°$ and $\gamma = 30°$, hence for both r is found from

$$r = 3.48 \cos^2 60° + 2.07 \cos^2 30° = 2.42$$

This value is smaller than both the observed values. If conversely from the numbers 2.59 and 2.85 α is calculated, then for N°. 4 53° is found, for N°. 6 42°, instead of 60°. It is not certain however that the differences are only caused by deviations from regular crystallisation. For, PERROT found for the density of his four best prisms numbers from 9,809 to 9,887, when the bismuth was always from the same source and had always been subjected to the same treatment; even in one and the same casting different densities were found. Hence it is possible that in the prisms too the density,

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and with it the resistance, varies in different points, as has been suggested by PERROT himself [1]). Accordingly the results with N°. 6 are only partially less satisfactory than those found with 4.

From the remainder of the crystalline piece another or seventh bar was cut, corresponding in original position as much as possible with N°.6. The resistance of this appeared to be 2.74, only slightly differing from N°. 6. Nevertheless in the further experiments this bar usually gave better results than N°. 6.

7. *The resistances along the axes in the magnetic field.* Without the magnetic field in the plane perpendicular to the principal axis all sets of two lines at right angles may be assumed to be axes. In the magnetic field a difference is possible between the direction which lies at the same time in the plane through principal axis and magnetic force and the perpendicular direction. We choose the original directions of the bars 2 and 3 as axes. In order that these directions shall remain axes also in the magnetic field, it is only necessary to suppose that the crystal revolves about the principal axis untill these directions coincide with the planes of symmetry determined by the magnetic force; nothing is thereby altered in the properties of the crystal as described with respect to the principal axis and the magnetic force. In the experiments the bars 2, 3 and 5 can then be used indiscriminately, for instance for measurements in the positions *Ob* and *Oc*, provided that care is taken to obtain a correct adjustment of the relative positions of principal axis, magnetic force and direction of current.

We first give only percentage increases of resistance, always in a field of 4600 C. G. S., and at 15° C.

Group I. Fig. 2a. Magnetic force ⊥ principal axis.

N°.	Position		
	Oa	*Ob*	*Oc*
1	13.0		
2		5.1	9.9
3		5.0	8.4
5		4.5	8.0

[1]) Arch. d. Sc. phys. et nat. (4) 6. p. 255. Septembre 1898.

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Each of the numbers under *Oa* and *Ob* is a mean of four, each of those under *Oc* of two corresponding positions, which usually showed only small differences.

For the construction of the new ellipsoid (dotted) the values for 1 and 5 were used. These give for the new axis the values:

$$(Oa)\ g_1^{90} = 1.60 \qquad (Ob)\ g_2^{90} = 2.16 \qquad (Oc)\ g_3^{90} = 2.12.$$

Hence the ellipsoid of conduction has now *three unequal* axes. In the plane perpendicular to the magnetic force the resistances are not proportionally increased. The simple hypothesis, formulated before [1]) and reconcilable with the former imperfect material, which assumed a proportional increase of resistance in this plane, must now be abandoned. However for the explication of the dissymmetry of the HALL-effect in bismuth, which was originally the object of this research, and for the description of the increase of resistance in the magnetic field this is a simplification. According to the researches of LEBRET and of myself the unequal increase of resistance in two perpendicular directions causes the dissymmetry. It has now become superfluous to take the direction of the magnetisation ($\mathfrak{J}$) into account in order to explain this inequality. As will appear from what follows, in each case where the principal axis is not perpendicular to the plate a disproportional increase of resistance, and with that dissymmetry, will be found.

In the figure the differences between the new axes and the old ones are drawn on a twice magnified scale in order not to render the drawing indistinct.

Group II. Fig. 2b. Magnetic force // principal axis.

N°.	Position	
	Od	*Oe* or *Of*
1	2.5	
2		5.0
3		4.4
5		2.9

[1]) Versl. d. Verg. 21 April 1897, d. 501. Comm. N°. 37. p. 18.

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The number under *Od* is a mean of four observations, the other numbers of two observations.

As there is no theoretical difference between N°. 2, 3 and 5 or the positions *Oe* and *Of* the latter are united in one column. So the ellipsoid remains one of revolution, while the whole variation is much smaller than in the preceding case. With the values for 1 and 5 the new axes become 1.68 and 2.17. With the value for 1 and the mean for 2 and 3, 1.68 and 2.15. For the figure we chose as new axes

$$(Od)\ g_1^0 = 1.68 \qquad (Oe,\ Of)\ g_2^0 = g_3^0 = 2.16.$$

In order to keep the drawing distinct it was here necessary to draw the variations to the scale of four.

Group III. Fig. 2c. Magnetic force and principal axis at an angle of 60°.

N°.	Position		
	Og	*Oh*	*Ok*
1	11.2		
2		4.1	9.1
5		4.0	7.6

Here also the three axes of the ellipsoid are unequal. With the values for 1 and 5 as a basis, the new axes become

$$(Og)\ g_1^{60} = 1.61 \qquad (Oh)\ g_2^{60} = 2.16 \qquad (Ok)\ g_3^{60} = 2.12,$$

hence only slightly differing from those in group I.

In the figure the differences are drawn on a double scale.

8. *Resistances along other directions in the magnetic field.* With regard to the differences between the results for corresponding bars even without the magnetic field, mentioned in § 6, it would not be allowable to directly compare resistances observed in the experiments of this § with calculated resistances, as in most cases the calculation will be based upon experiments with *other* bars. More is to be expected from a comparison between observed and calculated *increases*

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of resistance in the magnetic field and we will make the comparison in this manner. We should not however expect more than an approximate agreement.

For the calculation the following method was used: for each direction of experiment the resistance was calculated by means of the formula:

$$r = r_1 \cos^2 \alpha + r_2 \cos^2 \beta + r_3 \cos^2 \gamma,$$

in which for r_1, r_2 and r_3 the values applying without and in the magnetic field were consecutively substituted. From the two results a percentage increase of resistance for the direction α, β, γ was deduced, and this was compared with the percentage increase directly observed.

As an example of calculation:

Magnetic force $\perp$ principal axis. Direction On (fig. 2a).

$$\alpha = 60°, \quad \beta = 90°, \quad \gamma = 30°.$$

$$r_1 = 3.48 \quad r_2 = r_3 = 2.07$$

$$r_1^{90} = 3.93 \quad r_2^{90} = 2.16 \quad r_3^{90} = 2.24$$

$$r = r_1 \cos^2 60° + r_3 \cos^2 30° = 2.42$$

$$r^{90} = r_1^{90} \cos^2 60° + r_3^{90} \cos^2 30° = 2.66$$

Percentage increase of resistance $\frac{0.24}{2.42} = 9.9\ \%$.

Here follow the results for the three groups; the indices of the r's correspond to those of the g's.

$r_1 = 3.48 \quad r_2 = r_3 = 2.07 \quad r_1^{90} = 3.93 \quad r_2^{90} = 2.16 \quad r_3^{90} = 2.24$

Direction	α, β, γ	N°.	Perc. increase of resistance.			
			observed	calculated	along the axes of the corresponding ellipse	
					greatest	smallest
Ol	60°, 30°, 90°	4	10.2	7.5	13.0	4.5
»		6	9.2	»		
»		7	6.6	»		
Om	90°, 45°, 45°	5	5.5	6.3	8.0	4.5
On	60°, 90, °30°	4	8.7	9.9	13.0	8.0
»		6	10.2	»		
»		7	9.4	»		

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The most important deviations occur with the direction *Ol* where the increase of resistance for the axes is most different and accordingly a deviation of the direction of the axis has the largest influence. In each case the observed increase of resistance lies between the values of the last two columns.

Group II. Fig. 2b. Magnetic force // principal axis.

As there exists here no theoretical difference between the directions *Oe*, *Of* and *Op* and also between the bars 2, 3 and 5, for experimental purposes only the aequivalent directions *Oo* and *Oq* are left.

$r_1 = 3.48$ $r_2 = r_3 = 2.07$ $r_1^0 = 3.57$ $r_2^0 = r_3^0 = 2.15$

Direction	α, β, γ	N°.	Perc. increase of resistance.			
			observed	calculated	along the axes of the corresponding ellipse	
					greatest	smallest
Oo or *Oq*	60°, 30°, 90°	4	3.5	3.5	3.8	2.5
		6	5.1	"		
		7	4.0	"		

Group III. Fig. 2c. Magnetic force at an angle of 60° with the principal axis.

As mentioned before in § 7 in this case a doubt might arise whether the resistances will allow of a deduction from an ellipsoid and whether casu quo the axes will still be in the same directions as in both the former cases. An experiment which throws some light directly upon this question is the comparison of the increase of resistance in the directions *Or* and *Ov*. For the ellipsoid these are aequivalent; but for one of them the current is parallel to the magnetic force, for the other one the current flows at an angle of 60° to the magnetic force. The result of this experiment was:

	Or	*Ov*
with N°. 4	9.3	9.3
» 6	6.8	7.9
» 7	6.8	6.0

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Hence with N°. 4 the agreement is perfect; with 6 and 7 the deviations are in opposite directions. Therefore this result may be considered as confirming the supposition of an ellipsoid.

The results of the further experiments were:

$r_1 = 3.48$ $r_2 = r_3 = 2.07$ $r_1^{60} = 3.87$ $r_2^{60} = 2.15$ $r_3^{60} = 2.23$

Direction	α, β, γ	N°.	Perc. increase of resistance.			
			observed	calculated	along the axes of the corresponding ellipse	
					greatest	smallest
Or or *Ov*	60°, 30°, 90°	4	7.7	6.6	11.2	4.0
"		6	6.9	"		
"		7	6.6	"		
Os	90°, 60°, 30°	5	6.7	6.8	7.6	4.0
Ot	60°, 90°, 30°	4	7.3	9.1	11.2	7.7
		7	8.5	"		

The deviations in this case are certainly not greater than in the other groups, so that they may be considered as not contradictory to the supposition that in this case also the resistances in all directions can be found by means of a conduction-ellipsoid on the axes of symmetry.

9. This result would at once be explained if we were allowed to assume that, in the case of a magnetic force inclined with respect to the principal axis, the increase of resistance for each axis would be found as the sum of two increases, one caused by the component of the magnetic force parallel to, the second by the component perpendicular to the principal axis.

In order to test this hypothesis by means of the experiments it was necessary to know the function connecting the increase of resistance with the magnetic force in this bismuth. For this purpose I could use the formula deduced before [1])

$$\Delta r = \frac{C_2 M^2}{1 + C_1 \sqrt{M^2}}.$$

[1]) Versl. d. Verg. 25 Maart '99, p. 485. Comm. N°. 48, p. 4.

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As in most positions the increase was somewhat small for a reliable determination of the constants in this formula, I assumed that C_1 would have sensibly the same value for the various positions and axes, and only made some experiments for the direction *Oa*, in magnetic fields 2300, 3750 and 5800. These furnished for the constants the values

$$C_1 = 0.19 \qquad C_2 = 1.29.$$

In the experiments of group *III* the component of the magnetic force // principal axis was $4600\ cos\ 60° = 2300$, the component ⊥ principal axis $4600\ sin\ 60° = 3980$. Accordingly the increases of group *I* will have to be multiplied by

$$\frac{3.98^2}{4.60^2} \times \frac{1 + 4.60 \times 0.19}{1 + 3.98 \times 0.19} = 0.800 \text{ or } \frac{4}{5}$$

and those of group *II* by

$$\frac{2.3^2}{4.6^2} \times \frac{1 + 4.6 \times 0.19}{1 + 2.3 \times 0.19} = 0.326 \text{ or about } \frac{1}{3}.$$

So we find, using the values for N°. 1 and 5

Direction	*Og*	$\frac{4}{5} \cdot 13.0 + \frac{1}{3} \cdot 2.5 = 11.2$,	observed	11.2
»	*Oh*	$\frac{4}{5} \cdot 4.5 + \frac{1}{3} \cdot 2.9 = 4.6$	»	4.0
»	*Ok*	$\frac{4}{5} \cdot 8.0 + \frac{1}{3} \cdot 2.9 = 7.6$	»	7.4

The agreement here may be considered very good, it is however favoured by the fact that in this case the *same two* bars could be used for calculation and experiment. Hence the observations do not afford any reason to doubt the validity of the principle of superposition in this case.

10. The results of this research may be summed up as follows: In crystalline bismuth the HALL-coefficient is large for a magnetic force ⊥ principal axis, very small for a magnetic force // principal axis (same order of magnitude as in other metals), while the coefficient for a magnetic force in any direction can be deduced from those in both principal cases with the aid of an ellipsoid of revolution.

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Without a magnetic field the resistances in crystalline bismuth can be found for all directions by means of a conduction ellipsoid *of revolution* on the principal axis. (Axes in the ratio of 5 : 3).

In a magnetic field // principal axis there is an ellipsoid of revolution with comparatively slightly varied axes.

In a magnetic field ⊥ principal axis there is an ellipsoid with three more varied unequal axes.

In an arbitrary magnetic field there is an ellipsoid with three unequal axes which can be obtained by superposition of the variations of the axes in the principal cases.

The resistances in two directions at right angles in a plate of bismuth will generally increase *unequally* in the magnetic field, which explains the dissymmetry of the HALL-effect.

Physics. — J. C. SCHALKWIJK: "*Precise isothermals. I. Measurements and calculations on the corrections of the mercury meniscus with standard manometers*" (Communication N° 67 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

1. For the accurate investigation of isothermals of gases by means of piezometer tubes, into which mercury is forced, it is desirable to work with pretty large quantities of gas and to take care that the surface of the space it occupies is as small as possible with regard to its volume. For a given range of pressures we therefore desire to read the mercury meniscus in a tube the section of which is as large as is compatible with the accuracy of the adjustment and with the pressures which the piezometers have to resist. The correction for the capillary pressure to be applied to the pressure observed can only be applied with sufficient certainty when the piezometer tube is sufficiently large.

For such tubes, the volume of the meniscus may not in general be supposed to be equal to that of a spherical segment as it may allowably be considered in verry narrow tubes. This is the less permissible as the desired accuracy in the determination of the enclosed volume of gas is greater.

To attain in the measurements with the standard gasmanometers described in Communication N° 50 of the Physical Laboratory at Leiden, the high degree of accuracy for which they are designed, an investigation of the volume of the meniscus which shuts off the gas is indispensable. For, these piezometers are made to accurately determine together with the standard open manometers, described in

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N°. 44 of the Communications mentioned above, isothermals to within $^1/_{5000}$ — the manometer mentioned allowing absolute measurements of pressure to within $^1/_{10000}$.

Only when this accuracy is reached, we can arrive at some certain knowledge of several interesting questions in the theory of gases.

As with these piezometers the normal volume can be determined to within $^1/_{10000}$, so the volume of the compressed gas must also be exactly obtainable to within $^1/_{10000}$.

We will now demonstrate that in order to attain that accuracy the volume of the menisci in certain cases must be known to within 3 percent, while it will appear below (§ 9) that the deviation of the real volume from that of a segment of a sphere may amount to 20 percent.

The pressures of 4—8, 8—16, 16—32, 32—64 atmospheres are measured (see Communication N°. 50 p. 8) in tubes of 0.4, 0.28, 0.2 and 0.15 c.m. radius, each provided at its upper end with a widened reservoir. The tubes are calibrated by placing them entirely filled with mercury in a space of constant temperature (Communication N°. 50 p. 20) and by drawing off repeatedly a small quantity of mercury through a glas-cock, reading every time the level of the mercury in the tube and weighing the quantity run out.

During the calibration we must reverse the position of the tube, for in its proper position, owing to the large dimensions of the reversoir occupied by the gas at a pressure of 1 atm., it would form a gigantic thermometer, so that a small variation off temperature would bring about a perceivable displacement of the mercury surface. The displacement would influence most of all the calibration of the upper reservoir and the stem, which thereby as will be shown, would become less accurate than $^1/_{10000}$, and this upper reservoir is just the space in which the quantity of gas is to be compressed.

In the most favourable case — i. e. with the largest tube — the volume of the gas can become 20 c. c. And then only an error of 0.002 c. c. may remain, and as the volume of the large reservoir is 160 c. c., this error may already be caused by the expansion of the mercury, when an error of $^1/_{15}$ deg. C. has been made in the temperature. As in the calibration of a tube longer than a meter, these differences of temperature cannot be avoided without very special precautions, it is even in this most favourable case advisable to calibrate the tube in a reverse position, so that each time the mercury occupies chiefly that volume, which afterwards will be filled by the gas.

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But it is more necessary for the narrow tubes: in the fourth, for instance, the volume of the gas may fall to 2.5 c.c., while a volume of 175 c.c. is occupied by the mercury in the large reservoir of the tube. If the volume was measured in the upright position, the volume afterwards to be occupied by the gas would be measured as the difference of two mercury-volumes about 70 times as large, and in order to avoid an error of more than $^1/_{10000}$ in the gas-volume, we should have to be certain of the temperature to at least $^1/_{125}$ deg. C., a thing very nearly impossible for a tube of this length: therefore the calibration in the reverse position is absolutely necessary.

But in order to derive the volume of the gas above the mercury from the calibration of the tubes, we must know the exact volume of the meniscus; this is a fortiori necessary when the calibration has been made in the reverse position. For during this the meniscus points to the large reservoir, but during the observations to the small one. And so an error in the determination of the volume of the meniscus is felt doubly in the volume of the quantity of gas. Take for instance again the first tube, for which the volume of the meniscus is the most important and use in it the often occurring height 0.14 c.m., then the meniscus at a first rough approximation taken as a segment of a sphere would have a volume of 0.0365 cc. While we saw that an error in the gas volume may not exceed 0.002 cc. in this tube, an error larger than 3 percent may not be allowed in the volume of the meniscus.

In the following pages are communicated measurements, calculations, and graphical representations, which render it possible to determine the volume of the meniscus with the desired accuracy and to enable us to make the intended step forward in the accurate determination of isothermals. Successive calibrations of one tube which without the correction for the meniscus, failed to sufficiently agree, did so to within $^1/_{10000}$ after these corrections had been applied.

The measurements to be communicated concern the direct determination of the volume of some menisci. The calculations give an approximate solution of the differential-equation for the capillary surface in two limiting cases: *a* for very narrow tubes, and *b* for a very small ratio of the height to the radius of the tube, both with an approximate value of the surface-tension. By means of the graphical representation we derive from the menisci measured and from those calculated for the limiting cases, the value of the volume for each case. Moreover a test has been obtained § 7 by means of a graphical solution of the differential-equation [1]).

[1]) Compare also Sir W. THOMSON's Popular Lectures & Addresses I. p. 32.

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§ 2. *Determination of the volume of some mercury menisci by weighing.*

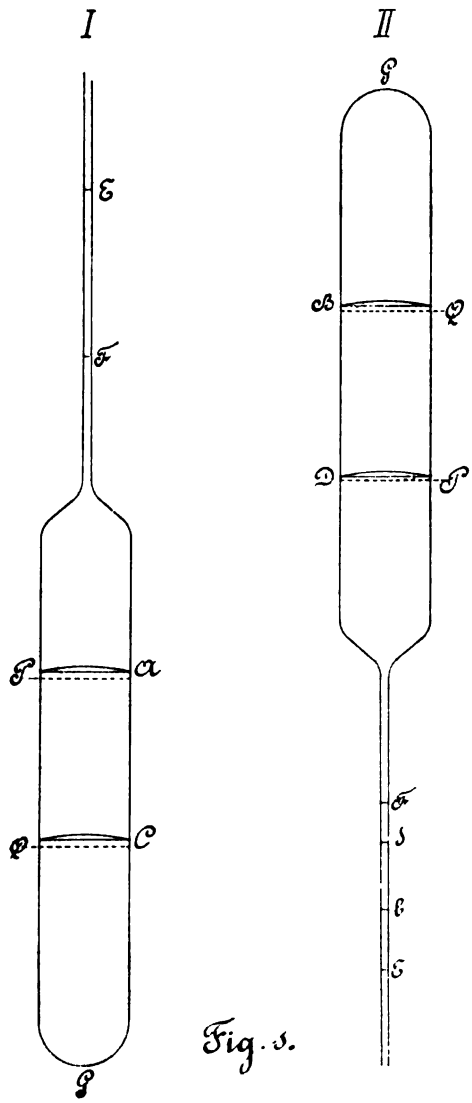

Fig. 3.

A tube of the bore for which we desire to know this volume at different forms of the meniscus, is provided at its upper end with a very narrow capillary tube and sealed at its lower end (see fig. 1). On the tube the divisions P and Q are made at about equal distances from the middle of the tube. It is well cleaned by boiling (comp. Communication N°. 50 § 5) and is filled in vacuo with purely distilled mercury, so that the mercury at 20° C. stands at E about 1 c.m. from the end of the capillary. In order to make measurements with the tube it is closed by sealing-wax and either with the capillary pointing upward (position I) or downward (position II) it is hung in a bath which is kept at 20° C. in a manner afterwards to be described. The height of the mercury surface with regard to the divisions must be read with a cathetometer. In order to avoid parallax the tube was hung so that the marks were on the side and the adjustment was made at the middle of these, which were seen as shallow grooves.

The mercury is weighed which must be forced out in order that after the tube is sealed again and put into the bath with a temperature t_F it should give the reading F in position I. Let the weight of this quantity be called H_{EF}. Again the mercury is weighed which is forced out to bring, after having a second time been sealed and placed in the bath, the meniscus in the position I at the temperature t_A to A, or in the position II at the temperature t_B in the wide tube at B and in capillary at b, which quantity we call

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H_{FA}, and also when further in the position I at the temperature t_C the meniscus is at C, or in the position II at the temperature t_D at D in the wide tube and at d in the capillary, i. e. the quantity H_{AC}. Finally we weigh the quantity H_{CG}, which is forced out last in order to empty the tube entirely.

In order to pass from the position I into the position II the capillary is opened, and the mercury transferred by gentle inclination to the position bB or dD without any loss, the capillary is then again sealed, after which the tube can be wholly placed in the position II.

The two marks P and Q were made in the immediate neighbourhood of the menisci to be formed, in order to enable us to determine accurately the distance of those menisci. For this distance is measured while the tube is immersed in the bath; now suppose that the tube and the glass wall of the bath are not perfectly parallel, or that in that glass wall the inner and outer sides are not perfectly parallel, then owing to the refraction of the light, the distance read on the cathetometer will not be equal to the distance of the menisci. Now by making the two marks P and Q we have only to measure in the water the very small distances from P to the meniscus very near to it and from Q to the meniscus quite near to it, so that only very small errors can occur, while the distance PQ outside the water can be determined with the greatest accuracy. By means of the temperatures t_F, t_E, t_A etc. and the weights H_{EF}, H_{FA}, H_{AC}, H_{CG} it is possible to determine at 20° C. the volumes of the glass reservoir corresponding to them; as these temperatures deviated at the highest 0.05 deg. from 20° C. a rough value for the apparent coefficient of expansion of the mercury is sufficient. Let V_{AC} be the volume between the planes going through the levels of the menisci A and C, and $V_{(AC)}$ the volume between the curved surfaces of the menisci A and C, and V_A the volume of the meniscus A etc.; σ the cross-section of the capillary; σ_{AC} the bore of the tube derived from V_{AC} and σ_{BD} the same bore derived from the volume V_{BD}.

So we get:

$$V_A + V_D = V_{(GA)} + V_{(FD)} - V_{FG} - V_{AD}.$$

$$V_B + V_C = V_{(GC)} + V_{(FB)} - V_{FG} - V_{BC}.$$

Let p_A be the height of the meniscus A, then we can always put:

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$$V_A = m + n p_A + x_1,$$

$$V_B = m + n p_B + y_1,$$

$$V_C = m + n p_C - y_1,$$

$$V_D = m + n p_D - x_1.$$

We then get the following values:

A. For the tube of 0.28 cm. radius:

$H_{EF} = 0{,}1046$ gr.	$V_{(EF)} = 0{,}00772$ c.m^2.	$EF = 3{,}415$ cm.
$H_{(EA)} = 14{,}8137$ »	$V_{(EA)} = 1{,}09352$ »	$bF = 0{,}934$ »
$H_{(EC)} = 20{,}0136$ »	$V_{(EC)} = 1{,}47735$ »	$dF = 0{,}385$ »
$H_{(EG)} = 35{,}2969$ »	$V_{(EG)} = 2{,}60553$ »	$AC = 1.527$ »
		$BD = 1.527$ »

From this we derive $\sigma = 0{,}00266$ c.m^2., and if first we equalize the volumes of the menisci:

$$\sigma_{AC} = 0{,}2513 \text{ c.m}^2.$$

$$\sigma_{BD} = 0{,}2505 \text{ »}$$

and so on an average $0{,}2509$ »

from which we get with sufficient accuracy $V_{BC} = 0{,}1305$ c.m^2.; $V_{AD} = 0{,}1305$ c.m^2.

And further

$p_A = 0{,}098,$	$m = -0{,}00212,$	$V_A = 0{,}01307 + x_1$ c.m^2.
$p_B = 0{,}100,$	$n = 0{,}155,$	$V_B = 0{,}01338 + y_1$ »
$p_C = 0{,}103,$		$V_C = 0{,}01384 - y_1$ »
$p_D = 0{,}113,$		$V_D = 0{,}01539 - x_1$ ».

If the values of x_1 and y_1 are small, as really will appear further on, then the volumes now found can serve to again determine the bore of the tube more accurately; we get: $\sigma_{AC} = 0{,}2519$; $\sigma_{BD} = 0{,}2518$ c.m^2. and from this follows again the more accurate values:

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$$V_A = 0{,}01305 + x_1 \text{ c.c.}$$
$$V_B = 0{,}01336 + y_1 \text{ »}$$
$$V_C = 0{,}01381 - y_1 \text{ »}$$
$$V_D = 0{,}01536 - x_1 \text{ »}$$

B. Tube of 0.38 c.m. radius. In quite a similar way we have found here:

$$\sigma_{AC} = 0{,}4584, \quad p_A = 0{,}104 \text{ cm.}, \quad V_A = 0{,}0277^5 + x_2 \text{ cc.}$$
$$p_B = 0{,}067 \text{ »} \quad V_B = 0{,}0166^5 + y_2 \text{ »}$$
$$p_C = 0{,}110 \text{ »} \quad V_C = 0{,}0301^5 - y_2 \text{ »}$$
$$p_D = 0{,}113 \text{ »} \quad V_D = 0{,}0310^5 - x_2 \text{ ».}$$

C. Tube of 0.41 c.m. radius. In this only two menisci have been determined, which chanced to have the same height, the measurement itself was less accurate:

$$\sigma = 0{,}525 \qquad p = 0{,}126 \qquad V = 0{,}0406.$$

§ 3. I intended to represent the volume of the meniscus as function of the principal dimensions by a surface. But as the surface which is obtained by drawing in three mutually perpendicular directions: 1. the radius of the tube, 2. the height of the meniscus, 3. the volume of the meniscus, would rise rapidly for increasing values of the radius of the tube, I have plotted not that volume itself, but its ratio to the bore of the tube; that ratio is called the mean height and is represented by the letter f. Moreover I have taken as ordinates: 1. the radius R of the tube, and 2. the ratio δ between the height p and the radius R.

We then obtain the following values from the menisci measured:

R	δ	f
0,2832	0,346	$0{,}0518 + x_1'$
»	0,353	$0{,}0530 + y_1'$
»	0,364	$0{,}0550 - y_1'$
»	0,399	$0{,}0611^5 - x_1'$
0,382	0,175	$0{,}0363 + y_2'$
»	0,272	$0{,}0605 + x_2'$
»	0,288	$0{,}0658 - y_2'$
»	0,296	$0{,}0677 - x_2'$
0.409	0,308	0,0733.

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§ 4. With these few data it would be impossible to obtain sufficiently accurately the surface which gives the mean height as a function of R and δ, if the theory did not allow us to determine that surface approximately near the limits $R = 0$ and $\delta = 0$. For the purpose I had in view a greater accuracy than 3 percents in the determination of the volume of the meniscus was not required, so I neglected in the calculation those terms whose influence remained below this value, as soon as it helped to simplify the calculation; for the sake of simplicity we have left uninvestigated other terms of perhaps still smaller influence but which did not give any difficulty in the calculation. We first will consider here the case that R is very small.

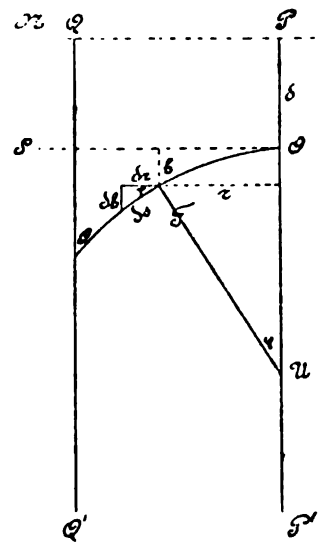

Fig. 2

Let PP' be the axis of the tube, QQ' the wall; the surface N the level on which the mercury stands outside the tube; OS the horizontal tangent plane to the top of the meniscus; let further r be the horizontal coordinate and h the distance below the surface OS; d the depression, H the surface tension, and s the specific gravity of mercury, then we have the well-known differential equation:

$$(\mathrm{d} + h)\, s = H \frac{\frac{1}{r}\frac{dh}{dr}\left\{1 + \left(\frac{dh}{dr}\right)^2\right\} + \frac{d^2h}{dr^2}}{\left\{1 + \left(\frac{dh}{dr}\right)^2\right\}^{3/2}}.$$

With very small values of R the depression d will always be great and the height h very small: and so the first member will differ little from d. Therefore I will in the first member replace h by some function of r, $f(r)$, which in a more or less approximate degree corresponds with the exact value h, and trace what influence that accepted function has on the solution following from the modified differential equation, assuming that $f(r)$ is in all cases small with respect to d.

For $f(r) = 0$, the differential equation has the known solution

$$h = \varrho - \sqrt{\varrho^2 - r^2},$$

a circle with a radius $\varrho = \frac{2H}{s\mathrm{d}}$.

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If further we assume $f(r) = k\,\mathrm{d}$, in which k is a very small constant we again get a circle with radius $\frac{\varrho}{1+k} = \varrho(1-k)$.

The increase of height becomes therefore:

$$h_k - h = \frac{h\,\varrho\,k}{\sqrt{\varrho^2 - r^2}}.$$

The greatest value has the relative increase of height at the wall, i. e. $\frac{k}{\sqrt{1-\left(\frac{R}{\varrho}\right)^2}}$. If we call θ, the angle of contact in the air then the last value becomes $\frac{k}{\sin\theta}$. Now as the minimum value of $\theta =$ about 51° that relative increase of height becomes $\frac{k}{0{,}777} = 1{,}29\,k$. As long as $k < 0{,}00777$, the relative increase of height at the wall is smaller than 1 percent, and then the relative error in the volume will be much smaller than 1 percent. As moreover the relative increase in height is proportional to k, a certain error in k passes proportionally over into the increase of height. Preceding considerations show that if we substitute for $f(r)$ in the differential equation an arbitrary function but so that its greatest value is always smaller than 0.777 percent of d while at the same time that function increases from 0 slowly and always in the same sense to that greatest value, the deviations in height and therefore certainly in the volume also remain smaller than 1 percent. We will avail ourselves of this result to judge of the limit to which we can continue this approximation.

It is obvious after we have obtained the first approximate solution $h_0 = f_0(r)$, the circle, when we suppose $f(r) = 0$, we look for the solution $h_1 = f_1(r)$, as a second approximation, which is obtained by putting in the first member of the differential equation $h = h_0 = f_0(r)$, and when this solution is obtained we look again for a new one, in which in the differential equation $h = h_1 = f_1(r)$ is put etc.

Difficulties however appear in the integration. In order to avoid these we may try for instance development in series, in which the first term in the development of $h_0 = f_0(r)$ in terms of r is first considered. It comes to this, that we do not assume $h_0 = f_0(r)$ as approximate solution but another $h_{01} = f_{01}(r)$, which contains

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only the 2nd power of r, i. e. which gives the meniscus as a first approximation the form of a parabola. If now however we assume a parabola, a better correspondence must be obtained by means of the parabola which passes through the top and the level of the meniscus, and therefore

$$h_{01} = \frac{p}{R^2} r^2,$$

in which p represents the height of the meniscus. The in this way simplified differential equation gives as first integral:

$$\frac{1}{2} d r + \frac{1}{4} \frac{p}{R^2} r^3 = \frac{H}{s} \frac{\frac{dh}{dr}}{\sqrt{1 + \left(\frac{dh}{dr}\right)^2}}.$$

This equation cannot as yet be integrated in a simple way, but can be easily made integrable by neglecting terms of the same order as we have done already. Therefore I take:

$$d = \frac{2H}{sR} (\cos \alpha - \eta R^2); \frac{s}{4H} \frac{p}{R} = \zeta \text{ and } r = x R,$$

in which then only R always remains very small. We then get:

$$h = \left[R \cos \alpha - \frac{\zeta}{\cos^2 \alpha} R^3 \right] . \frac{1 - \sqrt{1 - x^2 \cos^2 \alpha}}{\cos^2 \alpha} + \\ + \left(\frac{\zeta}{\cos^2 \alpha} - \eta \right) \frac{R^3}{\cos^2 \alpha} \left[\frac{1}{\sqrt{1 - x^2 \cos^2 \alpha}} - 1 \right].$$

By substituting in this $x = 1$, we have $h = p$, from which

$$\frac{1 - \sin \alpha}{\cos \alpha} = \delta \text{ and } - \zeta \sin \alpha + \zeta - \eta \cos^2 \alpha = 0.$$

From the first condition it appears that α is the angle of contact which we should have, if the meniscus was a segment of a sphere. And from the second condition follows then: $\eta = \frac{1}{2} \zeta (1 + \delta^2)$. Therefore:

$$h = \frac{R}{\cos \alpha} \left(1 - \sqrt{1 - x^2 \cos^2 \alpha} \right) - \\ - \frac{R^3 \zeta}{\cos^4 \alpha} \left[1 - \sqrt{1 - x^2 \cos^2 \alpha} - \sin \alpha \left\{ \frac{1}{\sqrt{1 - x^2 \cos^2 \alpha}} - 1 \right\} \right].$$

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eters.

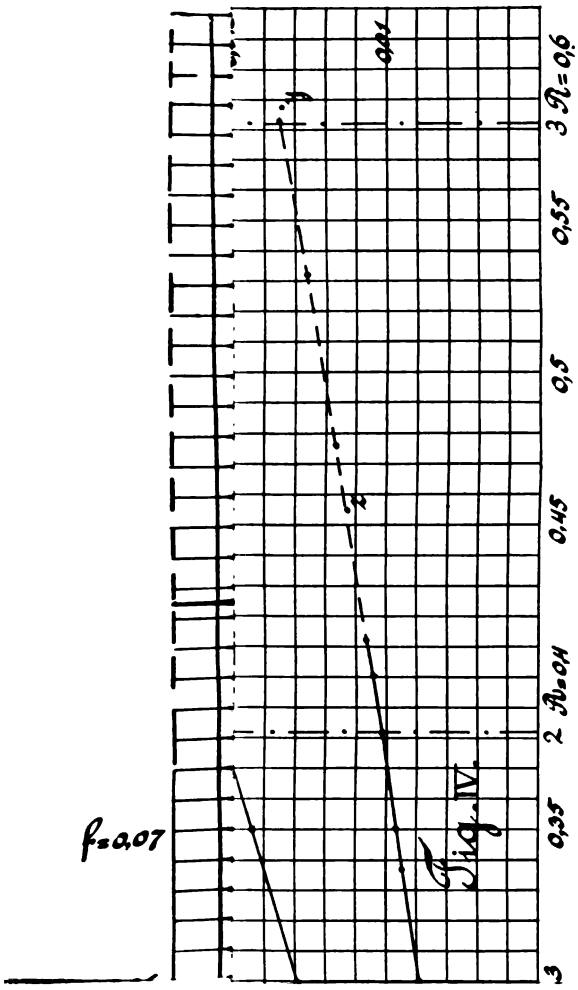

Fig. IV.

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In order to find out whether it is necessary to continue the work to obtain a third approximation I have calculated for a tube of 0,1 cm. radius (the widest to be considered here) the values of $f_0(r)$, the circle, $f_{01}(r)$, the parabola and $f_1(r)$, our second approximation, and have drawn them in fig. VII of the plate, for a value of $\delta = 0.35$, which often occurs with narrow tubes. I found:

x	Height for the circle represented by the line B.	Height for the parabola represented by the line C.	Second approximation represented by the line A.
0.1	0.000312	0.000350	0.000305
0.2	0.001203	0.001400	0.001006
0.3	0.002808	0.003150	0.002218
0.4	0.005054	0.005600	0.004333
0.5	0.008022	0.008750	0.006974
0.6	0.011711	0.012600	0.010270
0.7	0.016043	0.017150	0.014340
0.8	0.021337	0.022400	0.019634
0.9	0.027594	0.028350	0.026415
1	0.035000	0.035000	0.035000

The relative diminution of height according to the solution, obtained by introducing the parabola $f_{0,1}(r)$, amounts at a maximum to $^1/_6$ of the height which is obtained by putting $h = 0$. According to what we have found with the substitution $h = kd$, the relative decrease of height which would be found in the second approximation with $f_0(r)$, therefore will deviate from $f_1(r)$ at a maximum $^1/_6 \times$ the relative deviation which remains between $f_{0,1}(r)$ and $f_0(r)$. As the latter amounts at a maximum to $^1/_5$ we should not expect a greater relative deviation than $^1/_6 \times {}^1/_5 = {}^1/_{30}$. If further we take into consideration that the exact value of the meniscus and $f_1(r)$ are the same at the top and at the level of the meniscus, then it is obvious that the deviation in the volume will be much less than $^1/_{30}$ and thus is below the limit fixed above.

We now will determine the volume; this is:

$$\pi R^2 \int_0^1 2hx\,dx = \pi R^3 \left[\frac{1}{\cos\alpha}\left\{1 + \frac{2(\sin^3\alpha - 1)}{3\cos^2\alpha}\right\} - \frac{\zeta R^2}{3\cos^6\alpha}\left\{1 - \sin\alpha\right\}^3\right].$$

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If we substitute the values found for α and ζ then we find for the volume of the meniscus itself:

$$V = {}^1/_2\,\pi\,R^2\,p + {}^1/_6\,\pi\,p^3 + {}^1/_{96}\,\frac{s}{H}\,\pi\,p\,R^4\,(1+\delta^2)^3\,.$$

Here I have calculated for several values of δ the volumes of the meniscus for tubes of 0,04 and 0,1 cm. radius; for $\frac{H}{s} = 0{,}0354$ cm^2.

	δ							
Radius	0,05	0,1	0,15	0,2	0,25	0,3	0,35	0,4
0.04	0,000005	0,000010	0,000015	0,000020	0,000026	0,000031	0,000037	0,000042
0,1	0,000079	0,000158	0,000238	0,000321	0,000404	0,000489	0,000577	0,000668

§ 5. We will now consider the case that δ is very small. For this I will develop h in a series. If we substitute in the differential equation for h the series $\alpha r^2 + \beta r^4 + \ldots$. then we find by equalization:

$$\alpha = \left(\frac{s}{4\,H}\right) \mathrm{d}.$$

$$\beta = \frac{1}{(2\,!)^2}\left\{ 4\left(\frac{s}{4\,H}\right)^3 \mathrm{d}^3 + \left(\frac{s}{4\,H}\right)^2 \mathrm{d} \right\}$$

$$\gamma = \frac{1}{(3\,!)^2}\left\{ 72\left(\frac{s}{4\,H}\right)^5 \mathrm{d}^5 + 40\left(\frac{s}{4\,H}\right)^4 \mathrm{d}^3 + \left(\frac{s}{4\,H}\right)^3 \mathrm{d} \right\}$$

$$\partial = \frac{1}{(4!)^2}\left\{ 2880\left(\frac{s}{4H}\right)^7 \mathrm{d}^7 + 2520\left(\frac{s}{4H}\right)^6 \mathrm{d}^5 + 328\left(\frac{s}{4H}\right)^5 \mathrm{d}^3 + \left(\frac{s}{4H}\right)^4 \mathrm{d} \right\}.$$

We see that the n^{th} term itself of this development in series consists again of n terms, and these terms should first be summed before we can conclude to the convergency of the series. For this the general term should be found, which is very difficult. But still we see that this development in series will become valid when d is very small, so that terms of higher powers than the second can be neglected. This now is the case when δ is very small. But we cannot neglect d in the first member of our original

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differential equation, because h, and so the whole first member itself is small. But if δ is small $\frac{dh}{dr}$ must be small and so we can first begin to neglect the second member $\left(\frac{dh}{dr}\right)^2$ as compared with 1. Then we find by substitution:

$$\alpha = \frac{s}{4H}\,\mathrm{d}$$

$$\beta = \frac{1}{2^2}\left(\frac{s}{4H}\right)^2 \mathrm{d}$$

$$\gamma = \frac{1}{(3!)^2}\left(\frac{s}{4H}\right)^3 \mathrm{d} \text{ ect.}$$

These are exactly the coefficients which we get when we make the approximations mentioned in the solution of the complete differential equation. This series converges rapidly, as the ratio of the $(n\text{-}1)^{\text{th}}$ and n^{th} term is $\frac{1}{n^2}\frac{s}{4H}r^2$.

If we now suppose that in the differential equation we do not entirely neglect $\left(\frac{dh}{dr}\right)^2$ as compared with 1, but that we give to it the small constant value c, then we get:

$$\alpha = \frac{1}{2^2}\,\frac{s}{H}\,\mathrm{d}\left(1+c\right)$$

$$\beta = \frac{1}{4^2}\,\frac{s}{H}\,\alpha\left(1+\frac{5}{4}c\right)$$

$$\gamma = \frac{1}{6^2}\,\frac{s}{H}\,\beta\left(1+\frac{4}{3}c\right)$$

$$\partial = \frac{1}{8^2}\,\frac{s}{H}\,\gamma\left(1+\frac{11}{8}c\right) \text{ etc.}$$

We see thus that by the introduction of the small constant c all coefficients have become greater by an amount proportional to c, and that the series remains convergent, because the coefficient of c in the terms written as above, can become at the highest $^3/_2$ and so the limit ratio of two successive terms is the same as in the preceding case.

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For the same reason as in § 4 we shall approach more nearly to the exact solution if we substitute in the second member of the differential equation in the factor $1 + \left(\frac{dh}{dr}\right)^2$ for $\frac{dh}{dr}$ a function which has about the same course as the true value of $\frac{dh}{dr}$ and which yet gives easily summed series. For this also the parabola $h = \frac{p}{R^2} r^2$ is useful.

With slight approximation we then can put for the equation:

$$\frac{s}{H}(d+h) = \frac{1}{r}\frac{dh}{dr}\left\{1 - 2\frac{p^2}{R^4}r^2\right\} + \frac{d^2h}{dr^2}\left\{1 - 6\frac{p^2}{R^4}r^2\right\}.$$

If we substitute $h = \alpha_1 r^2 + \alpha_2 r^4 + \ldots\ldots$,
we find:

$$\alpha_1 = \frac{s}{4H}d.$$

$$\alpha_{n+1} = \frac{\alpha_n}{(n+1)^2}\left\{2n(3n-1)\frac{p^2}{R^4} + \frac{s}{4H}\right\}.$$

The limit ratio becomes therefore here $6\frac{p^2}{R^4}r^2$ and this ratio is according to our supposition very small. All coefficients are proportional to α_1 and of this the value is determined from

$$p = \Sigma\, \alpha_n R^{2n}.$$

In order to test the validity of this formula, we will apply it to our narrowest tube, for which $R = 0{,}2832$ c.M., for the value of $\frac{p}{R^2} = 0{,}35$ hence $p = 0{,}02807$ c.m. We then find:

$$\alpha_2 = 1{,}888\,\alpha_1,$$

$$\alpha_3 = 1{,}995\,\alpha_1,$$

$$\alpha_4 = 1{,}6\quad\alpha_1;$$

$$\alpha_1 = 0{,}3003;$$

$$d = 0{,}0424 \text{ c.m.}$$

$$h = 0{,}3003\,r^2 + 0{,}567\,r^4 + 0{,}599\,r^6 + 0{,}48\,r^8 + \ldots.$$

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and near the wall

$$p = 0{,}02807\,; \quad \frac{dh}{dr} = 0{,}2287\,; \quad \frac{d^2h}{dr^2} = 1{,}276.$$

If we substitute these values in the original differential equation the first member becomes:

$$\mathrm{d} + h = 0{,}0705$$

and the second member

$$\frac{H}{s} \frac{\frac{1}{r}\frac{dh}{dr}\left\{1 + \left(\frac{dh}{dr}\right)^2\right\} + \frac{d^2h}{dr^2}}{\left\{1 + \left(\frac{dh}{dr}\right)^2\right\}^{3/2}} = 0{,}0697.$$

Hence the difference is about 1 percent, so that for this case the formula can be applied, and the more so because we especially want the volume, in which the deviation will be still smaller because we can again secure coincidence at the top and at the level of the meniscus, by means of the formula $p = \Sigma\, \alpha_n R^{2n}$. For wider tubes the formula will certainly hold also, if the height is not greater than the one used here i. e. 0,028 cM., while for narrower tubes it will hold for the same value of δ, about 0.1. In order to test it still better I have calculated the first coefficients of the complete solution (§ 6, beginning) for the same tube. We find:

$$\alpha = 0{,}3003 \qquad \beta = 0{,}5567 \qquad \gamma = 0{,}632 \qquad \partial = 1{,}027$$

$$p = 0{,}02408 + 0{,}00358 + 0{,}00033 + 0{,}00004 + \ldots = 0{,}02803\ldots$$

differing very little from the accepted value 0,02807.

From $h = \Sigma\, \alpha_n r^{2n}$ we find for the volume of the meniscus:

$$V = \pi R^2 \left\{p - \Sigma \frac{\alpha_n}{n+1} R^{2n}\right\}.$$

In this case, for $R = 0{,}2832$ cM. and $\delta = 0{,}0991$ $V = 0{,}00373$ cc.

If however we had used the coefficients of the solution obtained from the complete equation then

$$V = 0{,}2519\,\{0{,}02803 - (0{,}01203 + 0{,}00119 + 0{,}00008 + \\ + 0{,}00001 + \ldots\} = 0{,}00371 \text{ cc.}$$

thus differing by less than 1 percent from the approximate value.

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We calculate:

for $R=0{,}2832$cM.; $\frac{p}{R^2}=0{,}25$ hence $p=0{,}0201$ and $\delta=0{,}0708$; $V=0{,}00265$cc.

» »= » »; »=0,15 » »=0,0120 » »=0,0425; »=0,00158 »
» »=0,382 »; »=0,2 » »=0,0292 » »=0,0765; »=0,00725 »
» »= » »; »=0,1 » »=0,0146 » »=0,0383; »=0,00362 »

For still smaller values of δ we may use the development in series, in which $\left(\frac{dh}{dr}\right)^2$ is wholly neglected as compared with unity. We get

$$h=\mathrm{d}\,\Sigma\frac{1}{(n!)^2}\left(\frac{s}{4H}\right)^n r^{2n}.$$

and for the volume of the meniscus

$$V=\pi p R^2\left\{1-\frac{\Sigma\frac{1}{(n!)^2(n+1)}\left(\frac{s}{4H}R^2\right)^{n-1}}{\Sigma\frac{1}{(n!)^2}\left(\frac{s}{4H}R^2\right)^{n-1}}\right\}$$

(To be continued.)

Physics. — H. A. LORENTZ. — "*The Theory of Radiation and the Second Law of Thermodynamics*".

§ 1. In his celebrated theoretical researches on the emission and absorption of rays of heat and light, KIRCHHOFF was led to introduce a certain function of wave-length and temperature which is independent of the particular properties of the body considered. This function, whose mathematical form later investigators have tried to determine, represents the ratio, at a definite temperature and for a definite wave-length, between the emission E and the absorptive power A of a body, both taken in the sense assigned to them by KIRCHHOFF; indeed, by his law, this ratio is the same for all bodies, being always equal to the emission of what KIRCHHOFF calls a perfectly black body.

§ 2. The function in question has yet another physical meaning. If a space which contains nothing but aether is enclosed by perfectly black walls of the temperature T, it will be traversed in all

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directions by rays, and the aether will thus be the seat of a certain amount of energy. We may consider this energy as made up of a large number of parts, each of them belonging to the rays of a particular wave-length, and, for a given state, this repartition of the energy over the radiations of different periods can only be effected in a single way. Hence, if for unit space, we write

$$f(T, \lambda)\ d\lambda$$

for the energy, as far as it corresponds to the rays of wave-lengths between λ and $\lambda + d\lambda$, and

$$\mu = \int_0^\infty f(T, \lambda)\, d\lambda$$

for the whole energy, the function $f(T, \lambda)$ will be wholly determinate.

Now, this function is intimately connected with the emission of the black walls, and from KIRCHHOFF's law it follows that the state of the aether which it defines may also be the result of the radiation of a body that is not black.

To begin with, the walls of the enclosure may be made on the inside perfectly reflecting, instead of perfectly black. If, then, a certain part R_1 of the enclosed space be occupied by a black body M of the temperature T, and the remaining part R_2 by aether, it is easily seen that the state characterized by $f(T, \lambda)$, if once existing in R_2, will not be disturbed by the presence of M, but will be in equilibrium with the internal motions of the ponderable matter. It will even be the only state having this property, and must therefore of necessity be produced by the body, provided the geometrical conditions are such that, after a certain number of reflections by the walls, every ray in the space R_2 must ultimately strike the body M.

KIRCHHOFF's law further proves that the equilibrium will continue to exist, if the black body is replaced by any other body M of the temperature T, whatsoever be its physical and chemical state and its properties. What is more, such a body will also *give rise* to the same state of radiation as the black body did before, at least if the above geometrical condition is again fulfilled, and if, besides, the body has some absorptive power, be it ever so feeble, and consequently some emissivity, for every wave-length that is represented in the radiation of the black body. This may safely be assumed.

The function $f(T, \lambda)$ is thus seen to have a second universal phy-

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sical meaning. The state of the aether to which it relates may for the sake of brevity be called the state corresponding to the temperature T.

§ 3. Since KIRCHHOFF's time great advances have been made in the investigation of the form of the function. By a most ingenious reasoning, founded partly on thermodynamic principles and partly on the electromagnetic theory of light, BOLTZMANN [1]) has shown that the total energy per unit of volume must be proportional to the fourth power of the absolute temperature, so that, if this is henceforth designed by T,

$$\int_0^\infty f(T,\lambda)\,d\lambda = CT^4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is a universal constant, whose numerical value will of course depend on the choice of the units.

A result that has been obtained by W. WIEN [2]) is likewise very remarkable. He found that $f(T,\lambda)$ is of the form

$$f(T,\lambda) = T^5\,\varphi(T\lambda) = \frac{1}{\lambda^5}\,\psi(T\lambda), \quad . \quad . \quad . \quad . \quad (2)$$

$\varphi(T\lambda)$ or $\psi(T\lambda)$ being a function of the product $T\lambda$. Evidently BOLTZMANN's result is contained in the latter law.

WIEN [3]) and PLANCK [4]) have also endeavoured to discover the form of the function φ, but we need not here speak of these researches.

§ 4. The experiments of PASCHEN, and those of LUMMER and PRINGSHEIM have furnished a very satisfactory verification of the laws, expressed by (1) and (2), and have thus confirmed the fundamental supposition that the second law of thermodynamics holds in this domain of physics, as well as the validity of the reasoning by which the two formulae have been established. In fact, I don't see that any but perhaps some far fetched objection could be raised against the theories of BOLTZMANN and WIEN. In my opinion, we cannot but recognize all that has been said as legitimate deductions

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[1]) BOLTZMANN, Wied. Ann, Bd. 22, p. 291; 1884.

[2]) WIEN, Wied. Ann., Bd. 52, p. 132; 1894.

[3]) WIEN, Wied. Ann. Bd. 58, p. 662; 1896.

[4]) PLANCK, Drude's Ann. Bd. 1, p. 116; 1900. Verhandl. der deutschen Physik. Ges. Jahrg. 2, p. p. 202, 237; 1900.

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from CARNOT's principle, but in so doing we are forced to a remarkable and, at first sight, somewhat startling conclusion.

The state of the aether which corresponds to a given temperature is characterized not only by the amount of energy per unit of volume, but also by at least one definite linear dimension. We may for instance fix our attention on the wave-length for which $f(T, \lambda)$ has its maximum-value, and which I shall call λ_m, or we may calculate a certain mean wave-length by means of the formula

$$\overline{\lambda} = \frac{\int_0^\infty \lambda f(T, \lambda)\, d\lambda}{\int_0^\infty f(T, \lambda)\, d\lambda}.$$

Now, the form of the function may very well be such that the ratio between λ_m, $\overline{\lambda}$ and what other lengths [1]) it might be deemed convenient to introduce, is expressed by definite numbers, but we have to explain for what reason one of these, for instance λ_m, has precisely the length that has been found for it by observation. In considering this question we shall have to take into account that, by WIEN's law, λ_m is inversely proportional to the absolute temperature.

We have good reasons for believing that, in so far as the aether is concerned, the phenomena may be exhaustively described by means of the well known equations of the electromagnetic field. If this be true, it cannot be the properties of the aether which determine the amount of energy and the preponderating wave-length, the velocity V of light being the only constant quantity which these equations contain. Hence, within the enclosure considered in § 2, the value of the energy per unit volume and that of λ_m must be forced upon the aether by the ponderable body M. But then there must exist between different bodies a certain likeness, expressible by the equality

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[1]) We might for instance, without decomposing the vibrations in the aether by means of FOURIER's theorem, define a length l by the formula

$$l^2 = \frac{[\alpha^2]}{\left[\left(\frac{\partial \alpha}{\partial x}\right)^2 + \left(\frac{\partial \alpha}{\partial y}\right)^2 + \left(\frac{\partial \alpha}{\partial z}\right)^2\right]},$$

in which α is one of the components of the dielectric displacement or the magnetic force, whereas the brackets serve to indicate the mean values, taken for a space whose dimensions are large in comparison with the wave-length, or with l itself.

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of numerical quantities; else it would be inconceivable that two bodies call forth exactly the same values of μ and λ_m. Without some conformity, of one kind or another, in the structure of all substances, the consequences of the second law and this law itself cannot be understood. If it did not exist, we could not even expect that a piece of copper and a mass of water for instance, after having been brought by contact into states in which they are in thermal equilibrium, would, under all circumstances, remain in these states, when exposed to their mutual radiation.

§ 5. It is by no means surprising that the validity of the rules of thermodynamics should require a certain similarity in the structure of different bodies, for in reality these rules do not teach us something about a single body, but always about two or more bodies and about the way in which these act on one another. The proposition that two bodies which, when brought into contact with a third one, do not interchange any heat with it, will also be in thermal equilibrium with each other, is clearly of this nature, and it is easily seen that our remark applies likewise to the law, that the absolute temperature is an integrating divisor of the differential expression for the quantity of heat, required for an infinitesimal change of state.

Let us suppose that an experimental investigation of the states of equilibrium of which a body (or a system of bodies) M_1, when considered by itself, is capable, has led to distinguish these states by the values of certain parameters $\alpha_1, \beta_1, \gamma_1 \ldots$ Then, an infinitely small change of state may be defined by the simultaneous increments $d\alpha_1, d\beta_1, d\gamma_1, \ldots$ If, in every case, we measure the amount of heat dQ_1 that has to be supplied to the body, say by determining the equivalent mechanical energy, we may establish an equation of the form

$$dQ_1 = A_1 d\alpha_1 + B_1 d\beta_1 + C_1 d\gamma_1 + \ldots\ldots, \quad \ldots\ldots \quad (3)$$

in which the coefficients $A_1, B_1, C_1, \ldots$ are known functions of $\alpha_1, \beta_1, \gamma_1, \ldots$ The integrating divisors

$$\Delta_1', \ \Delta_1'', \ \Delta_1''', \ldots, \quad \ldots\ldots\ldots \quad (4)$$

of which the expression (3) admits, and which we may imagine to be determined by an ideal mathematician, will also be functions of the parameters.

Next, let M_2 be a second body or system of bodies. Operating

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with this, as we have done with the first one, we shall be led to the introduction of certain parameters $\alpha_2, \beta_2, \gamma_2, \ldots$, to an expression, corresponding to (3), say

$$dQ_2 = A_2\, d\alpha_2 + B_2\, d\beta_2 + C_2\, d\gamma_2 + \ldots,$$

and to its integrating divisors

$$\Delta_2', \Delta_2'', \Delta_2''', \ldots, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

These will be functions of $\alpha_2, \beta_2, \gamma_2, \ldots$. Now, the proposition that the temperature is an integrating divisor, ascribes a particular signification to one of the functions (4) and one of the functions (5), the inequality or equality of these functions, calculated each for a determined state of the body, having to decide as to whether the bodies, taken in these states, and placed near each other will exchange heat or not. However, in calculating the functions (4), we have not even thought of the body M_2, and in forming the functions (5), we have not had in view the system M_1. Therefore, the two functions could not be involved in what happens in the mutual action of the two bodies, if these had nothing at all in common.

§ 6. In our ordinary molecular theories, which leave out of account the phenomena in the aether, the question is very simple. So far as we know, the total want of order in the molecular motions, precisely the state of things which justifies the introduction of the calculus of probabilities, is, in these theories, a sufficient ground for the general validity of CARNOT's principle. This irregularity in the motion of the ultimate particles seems to be the only common feature of different bodies that is required. It has been found sufficient to prove the proposition that the mean kinetic energy of a molecule is the same for all gases of the same temperature, a result, which is of the highest importance in the theory of molecular motion, and is likely to be so too in that of radiation. Indeed, it is to be expected that in studying the state of the aether, corresponding to the temperature T, we shall meet again with the same definite amount of energy, with which a molecule of a gas, of that temperature, is, in the mean, endowed, and which must also play a part in the internal motions of a liquid or solid body.

I shall denote by ω this mean kinetic energy of a gaseous molecule at the temperature T.

§ 7. We shall now return to the question what similarity in the structure of all ponderable matter must lie at the bottom of the

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thermodynamic theory of radiation. Evidently, a perfectly satisfying answer could only be furnished by an elaborate theory of the mecanism of emission and absorption, such as has not yet been worked out, though PLANCK [1]) and VAN DER WAALS JR. [2]) have published interesting researches in this direction. We may however attack the problem in a way that does not require a knowledge of peculiarities. By comparing two systems, both composed of ponderable matter and aether, and which are, in a wide sense of the word, „similar", i. e. such, that, for every kind of geometrical or physical quantity involved, there is a fixed ratio between its corresponding values in the two systems, I shall try to show that, in all probability, the likeness in question consists in the equality of the small charged particles or *electrons*, in whose motions modern theories seek the origin of the vibrations in the aether. We shall begin by supposing that, in passing from one system to the other, the dimensions, masses and molecular forces may be arbitrarily modified; then we shall find that the charges of the electrons must remain unaltered, if the second system, as compared with the original one, is to satisfy BOLTZMANN's and WIEN's laws.

The consideration of similar systems has already proved of great value in molecular theory. It has enabled KAMERLINGH ONNES to give a theoretical demonstration of VAN DER WAALS's law of corresponding states; moreover, the experimental confirmation of this law has taught us that a large number of really existing bodies may, to a certain approximation, be regarded as similar.

Of course, if the theory is also to embrace the phenomena going on in the aether, we have less liberty in choosing the systems to be compared. Since the properties of the aether cannot be changed, the velocity of light is not in our power, and the similarity implies that all other velocities must likewise be left unaltered.

§ 8. Let the first of the two systems be the one that has been considered in § 2: a ponderable body M, and, next to it, a certain space, filled with aether, both enclosed by walls that are perfectly reflecting on the inside.

Let the ponderable body be built up of a large number of small particles, each of which has a certain volume, so that the density

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[1]) PLANCK, Drude's Ann. Bd. 1, p. 69, 1900.

[2]) VAN DER WAALS JR., Statistische behandeling der stralingsverschijnselen. Dissertation. Amsterdam. 1900.

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of ponderable matter is finite everywhere. To these particles we shall ascribe an irregular "molecular" motion and the power of acting on one another with certain "molecular" forces.

We shall further suppose them — or some of them — to be electrically charged, and, for convenience' sake, we shall consider each charge to be distributed over a small space, with finite volume-density ϱ. This density may be treated as a continuous function, which sinks gradually into 0 at the surface of the electrons. Of course, if some of the particles have no charge, we have only to put for these $\varrho = 0$.

Finally, we shall take for granted that the aether pervades the space occupied by the particles, and that a dielectric displacement $\mathfrak{d}$ and a magnetic force $\mathfrak{H}$ may exist as well inside as outside a particle.

Then, if $\mathfrak{d}_x, \mathfrak{d}_y, \mathfrak{d}_z, \mathfrak{H}_x, \mathfrak{H}_y, \mathfrak{H}_z$ are the components of $\mathfrak{d}$ and $\mathfrak{H}$, and $\mathfrak{v}_x, \mathfrak{v}_y, \mathfrak{v}_z$ those of the velocity, we have the following equations [1]):

$$\left.\begin{aligned} \frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} &= 4\pi\left(\varrho\,\mathfrak{v}_x + \frac{\partial \mathfrak{d}_x}{\partial t}\right), \\ \frac{\partial \mathfrak{H}_x}{\partial z} - \frac{\partial \mathfrak{H}_z}{\partial x} &= 4\pi\left(\varrho\,\mathfrak{v}_y + \frac{\partial \mathfrak{d}_y}{\partial t}\right), \\ \frac{\partial \mathfrak{H}_y}{\partial x} - \frac{\partial \mathfrak{H}_x}{\partial y} &= 4\pi\left(\varrho\,\mathfrak{v}_z + \frac{\partial \mathfrak{d}_z}{\partial t}\right), \end{aligned}\right\} \quad \ldots\ldots \quad (6)$$

$$\frac{\partial \mathfrak{d}_x}{\partial x} + \frac{\partial \mathfrak{d}_y}{\partial y} + \frac{\partial \mathfrak{d}_z}{\partial z} = \varrho, \quad \ldots\ldots\ldots \quad (7)$$

$$\left.\begin{aligned} 4\pi V^2\left(\frac{\partial \mathfrak{d}_y}{\partial z} - \frac{\partial \mathfrak{d}_z}{\partial y}\right) &= \frac{\partial \mathfrak{H}_x}{\partial t}, \\ 4\pi V^2\left(\frac{\partial \mathfrak{d}_z}{\partial x} - \frac{\partial \mathfrak{d}_x}{\partial z}\right) &= \frac{\partial \mathfrak{H}_y}{\partial t}, \\ 4\pi V^2\left(\frac{\partial \mathfrak{d}_x}{\partial y} - \frac{\partial \mathfrak{d}_y}{\partial x}\right) &= \frac{\partial \mathfrak{H}_z}{\partial t}, \end{aligned}\right\} \quad \ldots\ldots \quad (8)$$

$$\frac{\partial \mathfrak{H}_x}{\partial x} + \frac{\partial \mathfrak{H}_y}{\partial y} + \frac{\partial \mathfrak{H}_z}{\partial z} = 0 \quad \ldots\ldots\ldots \quad (9)$$

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[1]) See f. i. LORENTZ, Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern. 1895.

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These, with $\varrho = 0$ everywhere outside the electrons, and if we add proper conditions at the reflecting walls, serve to determine the state of the aether, as soon as we know the motions of the electrons.

The energy of the aether per unit volume is given by

$$2\pi V^2 \mathfrak{d}^2 + \frac{1}{8\pi} \mathfrak{H}^2, \quad \ldots\ldots\ldots \quad (10)$$

and the components of the force, exerted by the aether on the electrons, will be for unit charge

$$\left.\begin{aligned} &4\pi V^2 \mathfrak{d}_x + \mathfrak{v}_y \mathfrak{H}_z - \mathfrak{v}_z \mathfrak{H}_y, \\ &4\pi V^2 \mathfrak{d}_y + \mathfrak{v}_z \mathfrak{H}_x - \mathfrak{v}_x \mathfrak{H}_z, \\ &4\pi V^2 \mathfrak{d}_z + \mathfrak{v}_x \mathfrak{H}_y - \mathfrak{v}_y \mathfrak{H}_x. \end{aligned}\right\} \quad \ldots\ldots \quad (11)$$

Besides these forces, there may be (molecular) forces of another kind, acting on the electrons.

§ 9. We have next to compare this really existing system S with a second system S', which perhaps will be only an imaginary one. Its enclosure is to be geometrically similar to that of S, the linear dimensions being a times what they are in the first system. By corresponding points in the spaces within the two enclosures, we shall mean points that are similarly situated, and to every instant in the interval of time, during which we consider the phenomena in S, we shall coordinate an instant for the second case, in such a way that the interval between any two moments in S' is a times the interval between the corresponding moments in S.

Let it further be assumed that, if at a particular instant ponderable matter or an electric charge is found at some point of one of the two systems, this will likewise be the case at the corresponding time and the corresponding point of the other system. As a consequence, the distribution of matter and of electric charge will be, at corresponding times, geometrically similar in the two cases, the dimensions of the particles in S' and their mutual distances bearing the ratio a to the corresponding quantities in S.

What has been said suffices to determine the internal motions in S', as soon as one knows those in S; the velocities will be the same in the two systems, because we have supposed the ratio of corresponding times to be equal to that of corresponding lengths. Of course, the motions in S and S' will present just the same degree of irregularity.

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Now, our description of the state of the second system will become complete, if we indicate, for each of the physical quantities involved, the number by which we must multiply its value in S, in order to obtain its value in S' at corresponding points and times.

Let this factor be b for the density of ponderable matter, c for the density of electric charge, and ac for the dielectric displacement and the magnetic force. Then, since the phenomena in the system S, which exists in reality, agree with the equations (6)—(9), those in S' will likewise satisfy these relations. Nor will the conditions imposed by the nature of the walls be violated. We may also remark that the formulae which are obtained for the two systems, if the motions are analyzed by means of FOURIER's theorem, will differ from each other only by the constant factors a and c. The ratio between corresponding wave-lengths, e. g. between the values of λ_m, will of course be a.

As to the motions we have attributed to the electrons in S', these will only be possible, if a, b and c satisfy a certain condition. The ratio of the accelerations being $\frac{1}{a}$, and that of the masses of corresponding elements of volume (or of corresponding particles) $a^3 b$, the forces acting on such elements must be in S' $a^2 b$ times what they are in S. Now, whereas the „molecular" forces may be supposed to be regulated according to this rule, the action of the aether on the electrons in S' has already been fixed by what has been said. The components (11) of the force on unit charge are, in S', ac times what they are in S, and for the charges of corresponding elements of volume the ratio is $a^3 c$. The factor for the forces exerted by the aether on such elements will therefore be $a^4 c^2$, and we must have the relation

$$a^2 b = a^4 c^2,$$

or

$$b = a^2 c^2. \quad \ldots\ldots\ldots \quad (12)$$

This being the only condition, we may imagine a large variety of systems S', similar to S, and which must be deemed possible as far as our equations of motion are concerned. The coefficients a and c having been chosen, and b calculated by (12), we should find, by (10),

$$a^2 c^2 \quad \ldots\ldots\ldots \quad (13)$$

for the ratio of the kinetic energies per unit volume, and

$$a^3 b,$$

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or, in virtue of (12),

$$a^5 c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)\,^1)$$

for the ratio of the kinetic energies of a molecule or an electron.

The latter number will at the same time be the factor by which we have to multiply the temperature T of S in order to obtain that of S'. Indeed, in the formulae (1) and (2), we may suppose T to be measured by observations in which radiation does not come into play, say by means of a thermometer; we may therefore apply the result of molecular theory that T is proportional to the mean kinetic energy of a particle.

§ 10. If we had only to satisfy the equations of motion, a and c might be arbitrarily chosen. We could then take

$$c = a^{-\frac{5}{2}}$$

and $b = a^{-3}$. By this the value of (14) would become 1 and that of (13)

$$a^{-3},$$

which might have any magnitude we like. In this way we should have got two systems S and S' of equal temperatures, but with different amounts of energy in the same space. This being in contradiction with the results, deduced from CARNOT's principle, the choice of a and c must be appropriately limited.

If the two systems we have compared with each other are to agree with BOLTZMANN's law, (13) must be equal to the fourth power of (14). From this we conclude

$$a^3 c = 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

that is to say, the charges of corresponding elements of volume,

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1) A moving charged particle produces in the surrounding aether an electromagnetic energy, which, for small velocities v, may be reckoned proportional to v^2. It may therefore be represented by $\frac{1}{2} k v^2$. The factor k plays the part of a mass, and may be called the electromagnetic or apparent mass, in order to distinguish it from the (true) mass in the ordinary sense of the word. Now, k is found to be proportional to the square of the charge, and inversely proportional to the dimensions of the particle. The condition (12) therefore means that the ratio between the true and the electromagnetic masses is the same in S and S'. There would be no necessity to introduce a condition of this kind, if there were no true mass at all; neither, if some of the particles had no charge, and the remaining ones no true mass.

We may also express the relation (12) by saying, that the ratio between the electromagnetic and the ordinary kinetic energy has to be the same in the two systems.

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and also those of corresponding electrons must be the same in S and S'.

If (15) is satisfied, the two systems will accord with WIEN's law, as well as with that of BOLTZMANN. In the first place, the ratio of the temperatures, for which we found the number (14), now reduces to

$$\frac{1}{a}.$$

As the values of λ_m are to each other as 1 to a, they are inversely proportional to the temperatures of the two systems.

We may remark in the second place that the repartition of the energy over the rays of different wave-lengths will be similar in the two systems. Consider for instance the rays in S whose wave-lengths lie between λ and $\lambda + d\lambda$; by WIEN's law, the energy in unity of volume, depending on them, is

$$T^5 \varphi(T\lambda)\, d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The corresponding rays in the second system have their wave-lengths between λ' and $\lambda' + d\lambda'$, if

$$\lambda' = a\lambda, \qquad d\lambda' = a\, d\lambda,$$

and, in order to calculate the energy in unit space which is due to these rays, we have only to multiply (16) by the factor (13), which becomes $\frac{1}{a^4}$, in virtue of (15). Now, one gets the same expression

$$\frac{1}{a^4} T^5 \varphi(T\lambda)\, d\lambda,$$

if, in (16), one replaces λ by λ', $d\lambda$ by $d\lambda'$, and the temperature T of S by the temperature $T' = \frac{T}{a}$ of S'. It appears from this that the distribution of energy over the different rays in S' is exactly what it ought to be by WIEN's law at the temperature of the system.

§ 11. What precedes calls forth some further remarks. It might be argued that two bodies existing in nature will hardly ever be similar in the sense we have given to the word, and that therefore, if S corresponds to a real system, this will not be the case with S'. But this seems to be no objection. Suppose, we have formed an image of a class of phenomena, with a view to certain laws that

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have been derived from observation or from general principles. If then, we wish to know, which of the features in our picture are essential and which not, i. e., which of them are necessary for the agreement with the laws in question, we have only to seek in how far these latter will still hold after different modifications of the image; it will not at all be necessary that every image which agrees in its essential characteristics with the one we have first formed corresponds to a natural object.

We have many grounds for expecting that a theory of radiation can be developed on the lines drawn in § 8. In such a theory we shall have to distinguish between the hypotheses concerning the uncharged particles, the ordinary molecular motions and forces, and those which relate to the electrons, their dimensions, masses and charges and the non-electrical forces which, conjointly with the electromagnetic ones, determine their motion. Now, it seems natural to admit that in a theory of radiation the hypotheses which relate to the electrons form the essential part of the explanation, and that all the rest may be freely modified within the limits indicated by the ordinary molecular theories.

If we had a right, likewise to change at will the dimensions of the electrons, their true masses and the forces to which they are subject, the considerations of § 10 would only leave room for the conclusion, that a definite magnitude of the electric charges must be reckoned among the essential features of our picture. One might however be of opinion that these dimensions, masses or forces contain already elements that are necessary parts of the theory. For instance, the electrons could have a fixed, constant diameter, the same in all ponderable matter. If this were the case, our factor a could not be different from unity, and the formulae (12) and (15) would give $b = 1$, $c = 1$. The system S' would be identical with S, and it would be impossible to learn anything from it. Again, the ratio between the densities of ponderable matter and of electric charge might be a universal constant. This would require $b = c$, and by (12) and (15) $a = b = c = 1$. The way in which we have treated the molecular forces acting on the electrons is also liable to objection. If a definite intensity of these forces were a requirement in the theory, it would be impossible so to regulate them, that they are in S' $a^4 c^2$ times as great as in S.

These remarks do not, however, invalidate the general conclusion, that the electrons in two ponderable bodies cannot be wholly different. We may even remark that, if it were found necessary to ascribe equal dimensions to the electrons of different bodies, it would

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be not unnatural to suppose them equal in all other respects. This latter hypothesis would likewise recommend itself as the simplest possible, in case we ought to assume a constant ratio between the masses and the charges, and a fixed relation between the above mentioned forces in different bodies would in its turn point with some probability to an equality of the electrons.

Of course I do not mean to say that all electrons in nature must be of one and the same kind. Anyways, there must be both positive and negative particles, and we may imagine any number of kinds of electrons we please. The conformity between different substances should in this case be attributed to the existence of each of those kinds, with their definite charge, in every body.

We must leave these questions for future research. The theory will also have to explain why the phenomena always depend on the temperature in the way expressed by the equations (1) and (2). It is true, we have compared cases in which the temperatures were not the same, but in those cases we had to do with different bodies, whose molecular weights were such, that the velocities of the particles were equal at the two temperatures compared. It will be necessary also to compare the same body at different temperatures, and this cannot be done by barely comparing similar systems.

§ 12. The question remains, on what quantities that are involved in the constitution of ponderable bodies the values of λ_m and the energy μ per unit space may be taken to depend. We have spoken of the dimensions, the masses and the electric charges of the electrons, or of a particular kind of electrons. These might be the same through all nature, and besides these there is the mean kinetic energy ω of a molecule at the temperature T. Now we may conceive different ways, in which λ_m and μ could be derived from these quantities. For instance, a given electric charge e, taken together with a given amount of energy ω, may determine a definite *length*. This follows at once from the „dimensions" of e and ω, but we may explain it as well by remarking that, if a charge e is uniformly distributed over a sphere of radius R, there will be an electrostatic energy

$$\frac{1}{2}\frac{e^2V^2}{R}$$

(e being expressed in electromagnetic units). Hence, if we desire this energy to have the value ω, the radius must be

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$$R = \frac{1}{2}\,\frac{e^2\,V^2}{\omega} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This is a length, entirely determined by e and ω, and it may be that λ_m bears always a fixed ratio to R. As to the energy per unit volume, it will probably be determined by some such condition as this, that the energy, contained in a cube whose side is λ_m, is in all cases the same multiple of ω [1]).

We may add that ω varies as T, and that therefore the line R, calculated by (17), will vary as $\frac{1}{T}$. Hence, the length of λ_m, if determined in the way we have indicated, will be found inversely proportional to the temperature, as we know it to be. Moreover, in accordance with BOLTZMANN's law, the energy in unity of volume would become proportional to T^4, if a cube, whose side varies as $\frac{1}{T}$, contained an amount of energy, which is itself proportional to the temperature.

I shall conclude by mentioning that Prof. PLANCK, after having found for the function $f(T, \lambda)$ the form

$$\frac{2\,V^2\,b}{\lambda^5}\,e^{-\frac{aV}{\lambda T}},$$

has calculated from experimental data the coefficients a and b contained in it, and has used these coefficients, together with the velocity of light and the constant of gravitation, for the purpose of establishing units of length, mass, time and temperature that are given by nature, without it being necessary to choose some standard body.

If the above considerations are to be trusted, this universal system of units would be based on the velocity of light, the constant of gravitation, the mean kinetic energy of a molecule and the properties of the electrons, present in all ponderable matter.

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[1]) What multiple this is, may be deduced from the observations on radiation, combined with what we know about the mass and the kinetic energy of a molecule. It is also implicitly contained in the considerations by which PLANCK terminates his last paper. By his formula, which, as he shows, agrees with the results of the kinetic theory of matter, I find that the energy of radiation in a cube whose side is $\bar{\lambda}$ (§ 4) amounts to a little more than 5,5 ω.

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Chemistry. — "*On the essential oil from the leaves of Alpinia malaccensis Rosc*". By Dr. P. VAN ROMBURGH.

In a communication [1]) on the occurrence of methyl cinnamate in the rhizomes of *Alpinia malaccensis*, I incidentally mentioned that the leaves of this plant yield an essential oil, which is likewise rich in this substance. Since then, I have prepared this oil in larger quantity and investigated the same jointly with Dr. TROMP DE HAAS, Assistant to the Agric. Chem. Laboratory of the Government Botanical Gardens at Buitenzorg.

From 700 Kilos. of fresh leaves, with the stalks attached, 1100 c. m. of oil were obtained. The yield is, therefore, 0.16 percent. The sp. gr. at 26° was 1.02. Rotation + 6.5°. When treated with aqueous soda 25 percent of the oil are not attacked, forming a liquid compound, the bulk of which boils from 160°—170°. This liquid may be isolated in a still more simple manner by treating the essential oil with steam; it then readily distils over whilst the methyl cinnamate, of which the oil consists to the extent of 75 percent, remains behind in a practically pure condition, and forms beautiful crystals on cooling.

By fractional distillation, the liquid portion yields a liquid, boiling from 158°—160°, having a sp. gr. of 0.857 at 26.5°. In a 200 m.m. tube it showed a rotation of 43° 20' to the right. The analysis and the vapour density agreed with that of a substance of the composition $C_{10}H_{16}$.

This hydrocarbon clearly belongs to the pinene group; with nitrosyl chloride it yields a compound which [2]), by the action of piperidine, gives pinene nitrolpiperidine melting at 118° — 119°.

Chemistry. — "*On the action of nitric acid on the esters of methyl-phenylaminoformic acid.*" By Dr. P. VAN ROMBURGH.

Some years ago, I have shown that by the action of nitric acid on the esters of phenyl-aminoformic acid, under definite circumstances, two or three NO_2-groups simply enter the benzene nucleus without any substitution of NO_2 for the amino-hydrogen, or liberation of the formic acid-residue taking place.

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1) Report of ordinary meeting Kon. Akad. v. Wetensch. 23 April 1898.

2) This nitrosylchloride compound does not, however, melt at 103° but at 108°. I also found that melting point for an analogous compound from the terpene from the leaves of *Myristica fragrans*.

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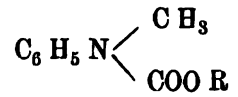
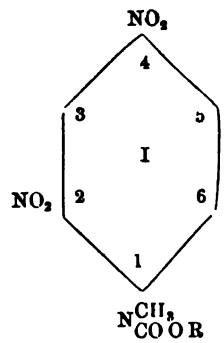
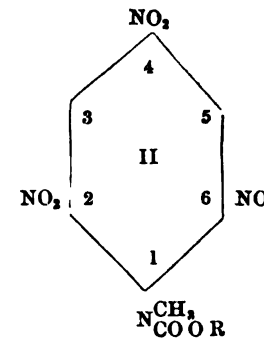
In continuation of that research, I have now studied the action of nitric acid on the methyl derivatives of the esters:



The possibility should exist here that, besides nitration of the nucleus, the formic acid-residue might be replaced by NO_2 with the formation of trinitrophenylmethylnitramine which is very stable towards nitric acid, or the methyl group might be replaced by hydrogen or, what is least likely, by NO_2.

The result of the research was, however, quite different from what was expected. The methyl group as well as the formic acid-residue remain intact and the reaction is limited to the introduction of NO_2-groups into the benzene nucleus. Whilst, however, when dealing with phenylaminoformic esters, it is an easy matter to introduce *three* nitrogroups into the nucleus, this is not successful with the methyl compound and only *di*-nitroderivatives are obtained of the formula I:





Trinitroderivatives of the formula II may however, be prepared by an indirect way, so that one is led to suppose that there exists a so called sterical obstacle to the introduction of the third NO_2-group in the place 6.

The methyl ester of methylphenylcarbamic acid was prepared by the action of methylaniline on the methyl ester of chloro-formic acid in the presence of water and obtained in the form of a nicely crystallising compound melting at 44°. The boiling point is situated at 243°. When its solution in sulpharic acid is added to very concentrated nitric acid a substance is obtained, which crystallises in beautiful glossy transparent crystals melting at 98°. This is the dinitroderivative.

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The ethyl ester of methylphenylcarbamic acid has already been prepared by GEBHARDT [1]) by the action of methylaniline on the ethyl ester of chloro-formic acid in ethereal solution. I also succeeded very well with the preparation in the presence of water. I found the boiling point 5° higher than that of the methyl ester.

By the action of nitric acid a product is obtained melting at 112° which is the dinitro-compound [2]).

Heating in sealed tubes with fuming hydrochloric acid at 150° breaks up both dinitrocompounds with formation of carbon dioxide, alkyl chloride and dinitromethylaniline $C_6 H_3 \overset{4}{NO_2} \overset{2}{NO_2} \overset{1}{NH} CH_3$, melting at 178°, which for the purpose of identification was treated with fuming nitric acid, which formed trinitrophenylmethylnitramine melting at 127°.

When both dinitroderivatives are boiled with fuming nitric acid they do not appear to become altered. Up to the present I have not succeeded in introducing a third nitrogroup.

As it did not seem without importance to ascertain whether the desired trinitrocompounds might not be prepared by another method. I have made the following experiments.

An aqueous solution of the potassium compound of the methyl ester of trinitrophenylcarbamic acid was treated with silver nitrate, which forms the sparingly soluble silver salt. This is then treated with methyl iodide in the presence of methyl alcohol. Silver iodide is formed, and from the methyl alcohol may be isolated a yellow compound, which after being recrystallised a few times, melts at 112—113° and is the desired trinitrocompound.

In an analogous manner, I prepared the ethyl ester, which melts at 65°.

That indeed the methyl group in these compounds is linked to the nitrogen of the aminogroup could be demonstrated by boiling them with a solution of potash which caused a liberation of *methylamine* which could be proved beyond doubt by the reaction with bromo-dinitrobenzene, which formed dinitromethylaniline melting at 178° and yielding, by treatment with nitric acid, trinitrophenylmethyl-nitramine melting at 127°.

The reaction with methyl iodide has, therefore, proceeded normally

$$C_6 H_2 . \overset{2.4.6}{(NO_2)_3} \overset{1}{N}\!\!<\!\!\begin{matrix} CO\,O\,R \\ Ag \end{matrix} + CH_3 J = C_6 H_2 \overset{2.4.6}{(NO_2)_3} \overset{1}{N}\!\!<\!\!\begin{matrix} CO\,O\,R \\ CH_3 \end{matrix} + Ag J$$

[1]) B. B. 17, S. 3042.

[2]) It is peculiar that this nitrated ethyl ester has a higher melting point than the corresponding methyl ester.

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Chemistry. — "*On the essential oil from Ocimum Basilicum L.*" By Dr. P. VAN ROMBURGH.

In the Botanical Garders at Buitenzorg are cultivated three varieties (?) of *Ocimum Basilicum L.* which, although containing essential oils of very different composition, seem not sufficiently to differ from a botanical point of view to make different species of them. The natives call them by the names of Selasih hitam, Selasih hidjau and Selasih Mekah (or S. besar).

The oil from the first one, which has dark-green leaves, has been prepared by me many years ago, the yield is, however, very small so that the material for a more extended investigation is still wanting.

As regards the oils of the two others, some preliminary communications will be made here.

From the variety Selasih hidjau, which is distinguished from the previous one by a light-green leaf, 0.2 percent (of the fresh herb) of an oil with a fennel-like odour is obtained by distillation with steam; this was investigated jointly with Dr. TROMP DE HAAS.

The specific gravity of this oil was 0.948 at 25°. On distillation the greater portion passes over between 214°—218°. Analysis and vapour density point to a substance of the composition $C_{10} H_{12} O$.

On treatment with alcoholic potash, anethol is produced whilst on oxidation with chromic acid, anisic acid is formed. The said properties lead to the conclusion that the chief constituent of this oil is methylchavicol, which has been found by DUPONT and GUERLAIN [1]) in French-, and by BERTRAM and WALBAUM [2]) in German-, and Réunion-Basilicum-oil.

In the lower fractions of the essential oil the probable presence of pinene could be ascertained.

From the fresh leaves of Selasih besar, I obtained 0.18—0.32 percent of an oil which possessed a strong odour of eugenol; the varying quantity probably depends on the age of the herb and to some extent on the duration of the distillation. Both the specific

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[1]) Bull. Soc. Chem. III, 19, p. 151.

[2]) Archiv d. Pharm. 235, S. 176.

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gravity and rotatory power varied with different samples (sp. gr. 0,890—0,940; rotation in a 200 m.m. tube —22°.5 to —36°).

The amount of eugenol varied from 30—46 percent.

The liquid remaining after removing the eugenol by dilute aqueous soda boils at 170°—250°, but its lower fraction cannot be separated at the ordinary pressure by fractional distillation as this alters its properties, which further investigation has shown. It may be readily isolated by treating the original oil with steam. One third part then readily passes over. A little eugenol which has been carried over is removed and the liquid distilled in vacuo. As chief product is then obtained a very agreeably smelling, optically inactive liquid which boils at 21 m.m. pressure at 73°—74°. The specific gravity is low, namely 0,794 at 22° and 0,801 at 15°, whilst the index of refraction was found $n_D = 1{,}4861$. Analysis and vapour density (according to HOFMANN) agrees with a substance of the composition $C_{10}H_{16}$. This substance to which I will give the name of *Ocimene* eagerly absorbs oxygen and then resinifies. If, for instance a little is introduced into a tube filled with oxygen and inverted over mercury, this is soon observed to rise and gradually fill the tube. On heating at the ordinary pressure, the boiling point, which is at first situated at 176°—178°, is gradually raised and after a few hours boiling under a reflux condenser in an atmosphere of carbon dioxide a liquid is obtained which boils at 195° at the ordinary pressure (at 93° at 25 m.m.), has a somewhat higher specific gravity and shows a stronger refraction [1]). A portion of the original liquid has, moreover, been converted into a product boiling at about 250°.

In its properties, this low-boiling liquid reminds of myrcene, isolated by POWER and KLEBER from Bay-oil, a so-called olefinic terpene (boiling point 67° — 68° at 20 m.m.; sp. gr. at 15° 0,8023, $n_D =$ 1.4673) which, however, as I convinced myself is distinguished from the same by its behaviour towards oxygen [2]).

I am still engaged with the study of these substances, also of a product with a higher boiling point from Selasih besar, which is probably a sesquiterpene.

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[1]) A preliminary determination gave $n_D = 1.5361$.

[2]) KLEBER and POWER, (E. GILDEMEISTER und FR. HOFFMANN „Die aetherische Oele" S. 668), state that myrcene gets polymerised after a week. I did not find this observation confirmed, for I could keep unaltered for months a specimen prepared by me from Bay-oil, kindly presented to me by the well-known firm of SCHIMMEL & Co. of Leipsic.

(January 23, 1901.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 26, 1901.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 Januari 1901 Dl. IX).

CONTENTS: Dr. J. J. BLANKSMA: "Organic polysulfides and the polysulfides of sodium". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 457. — N. SCHOORL: "On urea derivatives of sugars". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 459. — Prof. A. F. HOLLEMAN: "On the nitration of orthochloro- and orthobromobenzoic acid". (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 462. — Dr. J. H. ADRIANI: "Eutectic curves in systems of three substances of which two are optical antipodes". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 463. — Dr. H. B. HOLSBOER: "On heats of solution in general, that of $CdSO_4$, $^8/_3 H_2O$ in particular". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 467. — Dr. ERNST COHEN: "The Enantiotropy of Tin" VI. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 469. — Dr. G. BAKKER: "Contribution to the theory of elastic substances". p. 473. — J. C. SCHALKWIJK: "Precise Isothermals" I. (Continued). p. 481. (With one plate).

The following papers were read:

Chemistry. — Dr. J. J. BLANKSMA: "*Organic polysulfides and the polysulfides of sodium.*" (Communicated by Prof. C. A. LOBRY DE BRUYN).

In a former communication [1]) attention has been called to the fact that sodium disulphide lends itself to double decomposition both with o. and p. chloronitrobenzene and o. dinitrobenzene; the disulphides so formed may then (as was already known of tetranitro-

[1]) Proc. Royal Acad. of Amsterdam Nov. 25, 1899.

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diphenyldisulphide) be converted by nitric acid into the corresponding sulphonic acids.

On continuing this research it has been shown that Na_2S_2 is in general very adapted to double decomposition; a large number of aromatic and some more aliphatic disulphides have been prepared.

As these disulphides are nearly all readily converted into sulphonic acids by HNO_3, we possess in Na_2S_2 a general reagent for the preparation of sulphonic acids. This is of all the more importance because in this manner many sulphonic acids may be prepared which do not form by direct sulphonation.

In the previous communication it was suggested that substances with more than two sulphur atoms might be formed by direct substitution. This has now been proved to be true; with the aid of an alcoholic solution which contains 2 atoms of S for 1 mol. Na_2S, trisulphides are obtained, for instance from o. dinitrobenzene o. o. dinitrodiphenyl trisulphide: $NO_2.C_6H_4.S_3.C_6H_4.NO_2$ which on oxydation with nitric acid yields 1 mol. of sulphuric acid for 2 mols. of o. nitrobenzenesulphonic acid.

Tetrasulphides were further obtained both by direct substitution with the aid of Na_2S_4, and by removing, by means of iodine, two atoms of sodium from two mols. of sodium, dithiophenolate:

$$2\,NO_2.C_6H_4.SSNa + I_2 = NO_2.C_6H_4S_4C_6H_4.NO_2 + 2NaI.$$

This is, therefore, the application to a dithiophenolate of a method which is already known for monothiophenolates and was just the way according to which the aromatic disulphides could be prepared, for instance:

$$2\,C_6H_5SNa + I_2 = C_6H_5S_2C_6H_5 + 2\,NaI.$$

The above reaction is also comparable to the iodometric process where sodium tetrathionate is formed from thiosulfate.

Some general conclusions, which do not appear to be devoid of interest, may now be drawn from the above observations.

First of all this, that the di-, tri- and tetrasulphides of sodium really exist in an alcoholic solution. This appears from the di-, tri- and tetrasulphides obtained by double decomposition. (Special experiments abundantly proved that the aromatic di-, tri- and tetrasulphides could not be obtained by boiling the alcoholic solution of the mono- or disulphides with sulphur).

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A second conclusion of general interest is the one which relates to the constitution of anorganic polysulphides.

From the fact that sodium disulfide causes the formation of organic disulfides one mol. of which on oxidation with nitric acid splits up into two mol. of a sulphonic acid, it follows that in sodium disulfide one sodium atom is linked to each of the sulphur atoms; its constitution is, therefore, Na S—S Na and those of the organic disulfides R S—S R'. As, moreover, tetrasulfides are quantitatively formed from R S—S Na and iodine they may be assumed to have the constitution R S—S—S—S R' which supposes the existence in the molecule of a series of four atoms of sulphur linked to each other, comparable to those of carbon atoms. For the trisulfides the formula R—S—S—S—R' is then arrived at.

Finally, attention may be called to the fact that sodium disulphide acts as a deoxidiser on those nitro-compounds on which it does not act with double decomposition. The reaction takes place without formation of bye-products; so for instance m.m. dinitroazoxybenzene is formed from m. dinitrobenzene and p. p. dinitro-azobenzene from p. dinitrobenzene. The Na_2S_2 itself becomes $Na_2S_2O_3$ [1]).

For further particulars the dissertation should be consulted; its contents with a few additional observations will appear later on in the "Recueil".

Amsterdam, Dec. 1900.

Chemistry. — Mr. N. SCHOORL: "*On urea derivatives of sugars*". (Communicated by Prof. C. A. LOBRY DE BRUYN).

The investigation as to the existence of these compounds originated in the vain efforts to readily detect lactose in urine in a short time and to distinguish it from glucose. LOBRY DE BRUYN and ALBERDA VAN EKENSTEIN have attempted this by inverting the sugars and then reducing the same with sodium amalgam, the dulcitol formed from the galactose may be identified by its benzal-compound which is very adapted for this purpose. The negative result given by these experiments made it seem possible to me that on treating urine with a dilute acid the sugar combines with the urea and got removed as such.

[1]) See Proc. Royal Acad. of Amsterdam Oct. 27, 1900.

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From the following experiments it appears that under the influence of dilute acids glucose reacts with urea even at the ordinary temperature and more rapidly at an elevated one.

At 25°: 10 grams glucose, $2^1/_2$ gram of urea, dissolved in 5 pCt. sulphuric acid up to 50 c. c.

rotation at the commencement:		20° 20′
»	after 7 hours	20° 10′
»	» 24 »	19° 5′
»	» 48 »	17° 40′
»	» 101 »	15° 15′
»	» 580 »	7° 0′

At 50°: 5 grams of glucose, 1,6 gram of urea, dissolved in 5 pCt. sulphuric acid up to 50 c. c.

rotation at the commencement:		10° 10′
»	after 42 hours	6° 10′
»	» 96 »	5° 10′

I did not succeed in isolating from the so obtained reaction products a compound of glucose with urea, chiefly because the change seemed to be a limited reaction and because the excess of sugar formed a syrup and prevented a separation by solvents.

Therefore, another way was tried which led to a favourable result. Glucose (1 mol.) and urea (2 mols.) were warmed with 5 percent sulphuric acid for 20 days at 50°; the liquid was then freed from sulphuric acid by neutralisation with barium carbonate and filtered. By fermenting during 5 days the excess of glucose was removed and the now laevo-rotatory liquid evaporated to a syrup. After some days, a crystallisation took place, the crystals containing besides the excess of urea also a laevo-rotatory substance which was obtained pure by recrystallisation from alcohol and possessed the following properties.

Melting point: 206°. Rotation: $[\alpha]_D^{15} = -23°$ (1 percent solution).

Easily soluble in water, difficult in absolute alcohol, not or very little in ether, petroleumether, benzene, chloroform and acetone.

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Analysis:

Substance: 0,1705 gram, CO_2: 0,237 gram, H_2O: 0,0976 gram.

Nitrogen estimation (according to KJELDAHL):

Substance: 0,121 gram = 10.65 cc. $N/_{10}$ acid.

Found: C: 37,9 percent, H: 6,4 percent, N: 12,2 percent.

Calculated for $C_6 H_{12} O_5 . N . CO . NH_2$:

C: 37,8 percent, H: 6,3 percent, N: 12,6 percent.

On boiling the aqueous solution the rotation remained about constant; on warming with dilute acid it rapidly became positive.

FEHLING's liquid was reduced although less rapidly than by glucose. 0,040 gram of glucose-ureid reduced a quantity corresponding with the following amounts of $N/_{10}$thiosulfate:

after	1	minute	boiling:	8,7	cc.
»	2	»	» :	9,4	»
»	5	»	» :	10,1	»
»	10	»	» :	10,3	»

while the quantity of glucose (0,0324 gram) corresponding with 0,040 gram of glucose-ureid reduced copper to the extent of 10 cc. after boiling for two minutes.

Neutral copperacetate is not reduced by glucose-ureid. With a solution of phenylhydrazine in acetic acid it yields no osazone at first, but only on prolonged boiling.

An analogous compound of glucose with phenyl-urea [melting point 223°, $[\alpha]_D = -55°$ in 1 percent solution] was prepared in practically the same manner. The analysis gave:

Substance: 0,1596 gram, CO_2: 0,3014 gram, H_2O: 0,0875 gram.

Nitrogen estimation (KJELDAHL). Substance: 0,151 gram=9,9 $N/_{10}$ acid.

Found: C: 51,7 percent, H: 6.1 percent, N. 9,2 percent.

Calculated for: $C_6 H_{12} O_5 . N . CO . NH . C_6 H_5$:

C: 52,4 percent, H: 6,0 percent, N: 9,4 percent.

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The chemical properties proved to be analogous to those of the urea derivative.

Besides by heating in acid solution, it was found that the reaction of glucose with urea and phenyl-urea also takes place by melting these together at 100° — 150° and also by heating under pressure in methyl- or ethylalcoholic solution.

It was further noticed that lactose, galactose, mannose, arabinose and xylose also react with urea. On the other side the following derivatives of urea were tested as to their behaviour towards glucose: methyl-, phenyl-, benzyl-, symm. dimethyl, symm. diethyl- and symm. diphenyl-urea and it was noticed that the first three did react with sugar but the last three did not. On account of this and of the properties of the obtained glucose-ureids cited above, it may be assumed that at the condensation the carbonyl group of the sugar combines with one of the amido groups of urea with liberation of water:

$$\overset{|}{\underset{|}{C}} = \boxed{OH_2}\,N-CO-NH_2$$

and that these derivatives are, therefore, comparable with oximes and hydrazones.

It was also ascertained that thiourea and phenyl-thiourea react with glucose, although slower.

The study of these substances, which may also be important to physiology both by their possible occurrence in diabetic urine and with a view of a future synthesis of albuminous substances, will be continued.

Amsterdam, December 1900.

Chemistry. — Dr. A. F. HOLLEMAN: "*On the nitration of orthochloro- and orthobromobenzoic acid*" (Communicated by Prof. C. A. LOBRY DE BRUIJN).

MONTAGNE has shown in his dissertation [1]) that in the nitration of orthochlorobenzoic acid with nitric acid, there is formed besides the already known chloronitroacid ($CO_2H : Cl : NO_2 = 1 : 2 : 5$) a second mononitroacid which, however, he could not isolate in a pure condition. In this, I have succeeded by fractional crystallisation

[1]) Compare also Rec. **19**, 54.

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of the potassium salts. The K-salt of the main product crystallises first in thin long needles; in the very last motherliquors the bye-product has accumulated. This is liberated by hydrochloric acid and further purified by repeated crystallisation from dilute alcohol. It then has a melting point of 185°; in dilute alcohol it is a little less soluble than the main product.

In the nitration of orthobromobenzoic acid only a single mononitroacid has, as yet, been noticed, namely the acid ($CO_2H : Br. : NO_2 = 1 : 2 : 5$). Here, however, is also formed a second mononitroacid which may be also obtained by fractional crystallisation of the K-salts. After repeated crystallisation from dilute alcohol, it melts at 191°. Its solubility in this liquid is about equally great as that of the main product of the nitration.

The nitrogroup enters the place 3 both in the o-Cl- and the o-Br-acid, so that the structure of two bye-products is $CO_2H : Cl(Br) : NO_2 = 1 : 2 : 3$. This was proved by heating the acids with ammonia to 150° when from both the same nitroamidoacid is obtained ($CO_2H : NH_2 : NO_2 = 1 : 2 : 3$) which was identified by its melting point (204°), its solubility in water, benzene and chloroform and by the melting point of its ethyl ether (104°).

The quantity which is formed of both bye-products will be determined accurately.

Chemistry. — Dr. J. H. ADRIANI: "*Eutectic curves in systems of three substances of which two are optical antipodes*". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

In my dissertation "Systems consisting of optical antipodes" (Amsterdam, 1900) I mentioned briefly (p. 53) a paper by BRUNI (Rendic. Accad. dei Lincei, 9 April 1899, pg. 332) in which he describes a method of deciding whether an externally-compensated inactive substance is a conglomerate, a racemic substance or a pseudo-racemic mixed crystal. BRUNI-proposes to determine the eutectic point of a solution of one of the antipodes, to afterwards dissolve mixtures of the antipodes in known proportion in the same solvent and again find the eutectic points. If all mixtures from 100 percent *d*- to 100 percent *l*- are tested in this way such a point will be found for each mixture. These temperatures may be considered, for the solvent under consideration, as functions of the composition of the mixture of antipodes and a figure may

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be thus obtained from which the nature of the inactive substance can be deduced. If three curves (a, b, c or a', b', c', fig. I) are obtained one has to deal with a racemic substance; two curves (e, f, fig. II) are obtained when the inactive substance is a conglomerate of the antipodes; and one curve (g, h or i, fig. III) when one has got mixed crystals.

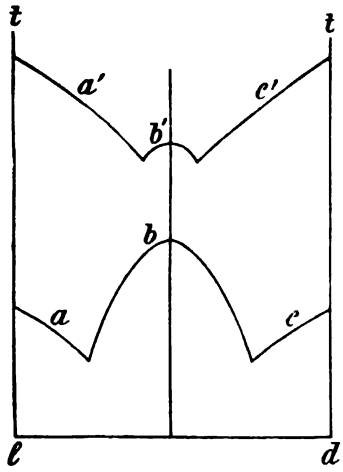

Fig. 1.

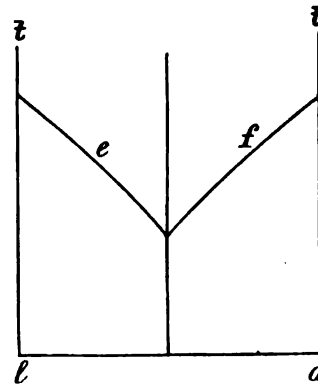

Fig. II.

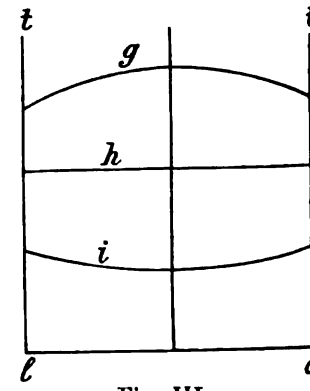

Fig. III.

BRUNI appears to have had in mind only aqueous solutions, but I fancy that the advantages of this method will be more particularly apparent when substances with a higher melting point are used as solvents. If a number of different compounds with different melting points are employed as third substance, a series of eutectic curves is obtained for the same system of antipodes, and the nature of the inactive substance at different temperatures may thus be elucidated. Because if with the same system two solvents are taken, of which one has a higher melting point than the other it will be found in general that the first line of eutectic points is situated at higher temperatures than the second. It may, therefore, happen that the first line has a character different from that of the second because the inactive substance at the first set of temperatures is racemic and at the second set a conglomerate or a mixed crystal. By now varying the third substance until the eutectic line at a given set of temperatures has been found, it will be possible to answer the question as to the nature of the inactive substance at a definite temperature or at least in a definite temperature zone. The method of BRUNI has not yet been applied; I, therefore, resolved to try it on camphoroxime, which I had already previously examined. I had found that above 103° i-camphoroxime must be looked

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upon as a mixed crystal, below 103° as a racemic substance. As third substance it is necessary to take one which has no chemical action on the oxime, may be obtained perfectly pure, crystallises on cooling in a form clearly distinguishable from the oxime and does not form mixed crystals with it: napthaline, phenantrene, benzoïn and anthracene were used. None of these substances acts chemically on camphoroxime; it is only when this condition is fulfilled that the point of change of the oxime is not altered by the admixture. Moreover, none of these substances forms mixed crystals with the oxime; this is also a condition for the unchangeability of the point of change.

The temperature at which the crystals of the oxime and the third substance melted simultaneously was taken as the eutectic temperature. This temperature was sometimes difficult to determine; easiest with napthalene. The determination was done in the apparatus first described by VAN EYK (Dissertation pg. 26). First, by determining the whole melting line, the eutectic point of the *d*-oxime with the third substance was found; in the determination of the other eutectic points the investigation of the whole of the melting line was superfluous, for the relation oxime: third substance at the eutectic point remained nearly constant with the different mixtures of *d*- and *l*-oxime, so that only a small part of the melting line needed to be examined in the neighbourhood of the eutectic point.

The results are as follows:

Eutectic Temperatures.

% d-	% l-	Napthalene m. p. 81°,4	Phenanthrene m. p. 99°,4	Benzoïn m. p. 137°,0	Anthracene m. p. 213°.
100	0	61°.0	76°.2	100°.2	109°.2
95	5	60 .0	—	—	—
90	10	59 .6	75 .6	99 .1	107 .6
80	20	59 .2	74 .9	98 .2	106 .8
75	25	59 .4	—	97 .8	—
70	30	60 .1	74 .2	97 .4	106 .2
65	35	60 .8	74 .8	—	—
60	40	61 .3	75 .6	97 .0	105 .1
50	50	61 .9	76 .2	97 .2	105 .6

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Of the eutectic lines, only the one half of 100 percent *d.* to 50 percent *d.*—50 percent *l.* has been investigated; the other half which is perfectly symmetrical with this has been dotted in the figures to give a better view.

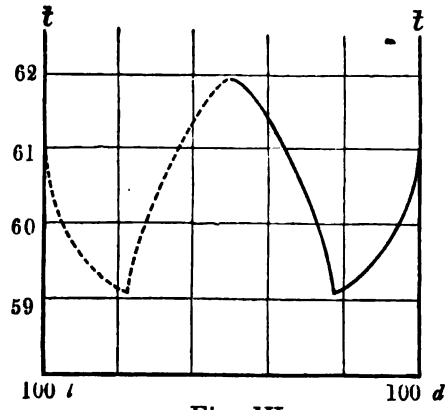

Fig. IV.
Naphtalene.

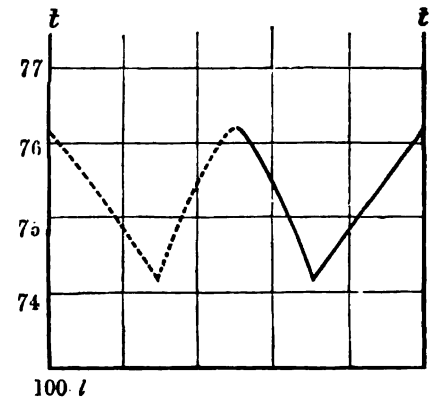

Fig. V.
Phenanthrene.

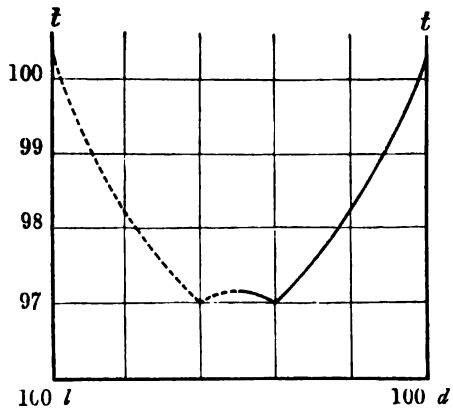

Fig. VI.
Benzoïn.

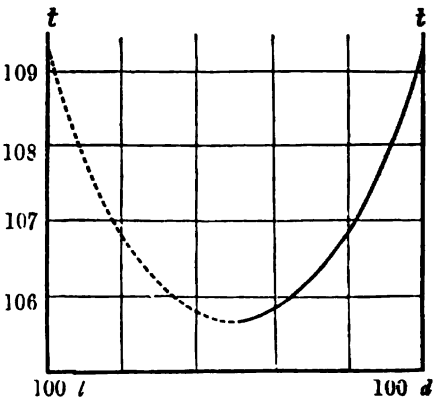

Fig. VII.
Anthracene.

These results confirm on the one hand the theoretical views of BRUNI and on the other hand the results which I had previously obtained with camphoroxime. The lines show that near to 60°, the eutectic point of the *i*-oxime is situated higher than that of the antipodes; at that temperature the solubility of the *i*-substance will be as a rule smaller than that of the antipodes as is also the case at the ordinary temperature with different solvents. At a higher temperature this difference becomes smaller; when nearing 76° (phenantrene)the eutectic points of the antipodes and the *i*-substance coincide; at higher temperatures this point has become lower in

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the *i*-form than in the antipodes. It may, therefore, be suspected that at that higher temperature the solubility of the *i*-form in different solvents will be greater than that of the active forms.

The line obtained with benzoin as third substance shows that the racemic compound still exists at 97°.2; the zone is, however, very restricted. Finally, at a still higher temperature the racemic compound has disappeared; the investigation with anthracene as third substance gave a continuous curve with a minimum at 50 percent *d.*—50 percent *l.* At 105°.6 the *i*-oxime must, therefore, be regarded as a mixed crystal of equal quantities of the active oximes.

This is quite in concordance with my previous investigations on camphoroxime, the results of which have been communicated in the report of the meeting of June 24, 1899.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents the dissertation of Dr. H. B. HOLSBOER: "*On heats of solution in general, that of* $CdSO_4, {}^8/_3 H_2O$ *in particular*" making the following communication regarding it.

Since 1884 it has been recognised that the calculation of the course of the solubility curves of solid substances in liquids as functions of temperature requires a knowledge of the so-called theoretical heat of solution, that is the heat of solution of the solid substance in its saturated solution. In 1885 I discovered a graphic construction by means of which this quantity, which cannot be determined experimentally, may be obtained from the curve of the heats of solution in different quantities of solvent. Later on VAN DEVENTER and STACKELBERG devised methods of calculating the same quantity from such determinations.

For salts whose saturated solutions are very dilute, the theoretical heat of solution differs but little from that in pure water; for salts with large solubility the sign may even differ. With some salts a minimum of solubility is shown at a definite temperature, the solubility, therefore, first decreases with an increase of temperature and then increases when past the minimum. On the first part of the curve the theoretical heat of solution must, therefore, be positive, on the second part negative and *nil* at the temperature of the minimum.

Up to the present, this change of sign of the evolution of heat has not been accurately proved to occur in any such case. Dr. HOLSBOER has investigated cadmium sulphate with ${}^8/_3$ mol. of H_2O

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which shows a minimum of solubility at 15°. He determined accurately the heat of solution of this hydrate in much water at 15° and also the heats of dilution of all kinds of solutions beginning with the greatest possible concentration. He further determined the specific heats of a series of solutions and of the solid salt, so that the heats of solution of solid salt in varying quantities of water at different temperatures could be calculated from the values at 15°. He obtained the following results.

Heat of solution of $CdSO_4\ ^8/_3\ H_2O$ in $(x—^8/_3)\ H_2O$.

x	5°	10°	15°	20°	25°
400	2075	2303	2530	2758	2985
200	2194	2306	2418	2530	2642
100	2118	2203	2288	2373	2458
50.6	2013	2065	2118	2170	2223
30.6	1835	1876	1918	1959	2001
20.6	1657	1645	1633	1621	1609
15.6	1405	1332	1258	1185	1111
13.6	1061	966	870	775	679

The saturated solutions contain, at the temperatures given: 15.03, 15.10, 15.17, 15.10, 15.03 H_2O.

The determinations of the heats of solution go beyond these concentrations. It was, therefore, easy to deduce the theoretical heat of solution from the course of the curves for the ordinary solutions in the immediate neighbourhood of the point corresponding to the saturated solution.

The following results were obtained:

Theoretical heat of solution.

5°	+	219 cal.
10°	+	165 »
15°	+	3 »
20°	—	620 »
25°	—	1221 »

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The agreement between the signs of the heats of solution and the course of the curve of solubility and the position of the minimum is very good.

The influence of temperature on the heat of solution is also very considerable.

It appears also from the table of the ordinary heats of solution that with dilute solutions the heat evolved increases with the temperature, owing to the fact that the specific heat of the solution is smaller than the sum of the values for solid salt and water. With concentrated solutions the reverse is the case. From this it follows that there must be a concentration where the heat of solution is independent of the temperature because the specific heat of this solution is equal to those of solid salt + water.

This appears to be the case with a solution with 22.5 H_2O.

In the graphic representation all the heat of solution curves intersect each other at the point corresponding to this concentration. For want of investigation of concentrated solutions, this peculiarity, which no doubt occurs with many substances, has up to the present escaped notice.

Chemistry. — Dr. ERNST COHEN: "*The Enantiotropy of Tin*" (VI) (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

Contributions to the history of grey Tin.

1. In the journal *Prometheus* [1]) E. KRAUSE referring to my previous investigations on the Enantiotropy of Tin [2]) makes the following communication: "Schon die Alten wussten, dass dieses weiche Metall, welches „schreit", wenn man es biegt, seine Mucken habe und der Verfasser eines mit Recht oder Unrecht dem ARISTOTELES zugeschriebenen Buches (*de Mirabilibus Auscultationibus* Cap. 51 Edit. BECKMANN) sagt: das keltische Zinn habe unter anderen merkwürdigen Eigenschaften auch die, nicht bloss (wie die anderen Metalle) in der Wärme zu schmelzen, sondern auch eintretender Frost bewirke dasselbe.

Auch PLUTARCH in den *Tischreden* (VI, 8) berichtet von in strengen

[1]) Jahrgang XI, 44, S. 701 (1900).

[2]) These Proceedings 1899 and 1900 also Zeitschrift für phys. Chemie 30, 601 (1899) 33, 57 (1900) 35, 588 (1900).

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Wintern herabgestürzten Bildsäulen, weil das Metall, mit dem es in den Postamenten vergossen, durch den starken Frost geschmolzen sei.

Diese Thatsachen waren so bekannt, dass ARISTOTELES sich um eine physikalische Deutung bemühte. Das Metall, sagte er, ziehe sich im Froste so stark zusammen, dass die in seinen Poren enthaltene Wärme es durch die Zusammenpressung zum schmelzen bringe. Wie alles, was ARISTOTELES sagte, wurde dieser Angabe bis zur neueren Zeit Glauben geschenkt, und noch MONTAIGNE führt die Frost- und Hitzeschmelzung des Zinns zum Beweise dafür an, „dass sich die Extreme berühren".

As the question whether the Ancients were acquainted with the peculiar phenomenon shown by tin at low temperatures, interested me very much, I have endeavoured to find further particulars in connection with KRAUSE's communication.

It is only through the kind assistance of Prof. SPEYER of Groningen, to whom I here wish to express my hearty thanks, that it has been possible to control this matter; to him I am principally indebted for the following particulars.

2. In ARISTOTLE (or Pseudo-ARISTOTLE), *Περὶ θαυμασίων ἀκουσμάτων* 50, the following passage is found [1]) ***Τὸν κασσίτερον τὸν κελτικὸν τήκεσθαί φασι πολὺ τάχιον μολίβδου· σημεῖον δὲ τῆς εὐτηξίας, ὅτι τήκεσθαι δοκεῖ καὶ ἐν τῷ ὕδατι· χρώζει γοῦν, ὡς ἔοικε, ταχύ. τήκεται δὲ καὶ ἐν τοῖς ψύχεσιν, ὅταν γένηται πάγη, ἐγκαταλειομένου ἐντός, ὡς φασί, καὶ συνωθουμένου τοῦ θερμοῦ τοῦ ἐνυπάρχοντος αὐτῷ διὰ τὴν ἀσθένειαν.***

It is said that Celtic tin melts much more quickly than lead. A proof of the fusibility is the statement that it also melts in water; apparently it seizes [2]) quickly. It also melts in the cold when frost has set in, because, as is said, the heat contained in it is inwardly confined and compressed on account of its weakness.

3. The passage from MONTAIGNE cited by KRAUSE is found in his *Essais des vaines subtilités* [3]): L'extreme froideur, et l'extreme

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[1]) Bibliotheca scriptorum graecorum et romanorum Teubneriana, Lipsiae 1888. Editio OTTO APELT.

[2]) Prof. SPEYER in commenting on the translation of *χρώζει* by *seizes* says: this translation does not satisfy me. The word means to touch, to catch, to stain, but *χρώζει* is active and I cannot see how it could mean here "it discolours". I am more inclined to believe that the idea is "it is sensitive to outside influences".

[3]) I am quoting a Parisian edition (DESOER, librairie, rue Christine 1818). Nouvelle Edition, livre premier, LIV, pag. 104.

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chaleur cuisent et rotissent: Aristote dict que les cueux de plomb se fondent et coulent de froid et de la rigueur de l'hyver, comme d'une chaleur vehemente.

At this passage the editor adds in a note: "Ici MONTAIGNE ne rapporte pas exactement la pensée d'ARISTOTE, qui, après avoir dit que l'étain des Celtes se fond plutôt que le plomb, puisqu'il se fond même dans l'eau, ajoute: L'étain se fond aussi par le froid quand il gèle etc. *de mirabilibus auscultationibus* p. 1154 Edit. Paris, Tome 1.

That MONTAIGNE made a mistake when he cited ARISTOTLE in this place appears from the fact that what he attributes to ARISTOTLE [1]) may be read in PLUTARCH (*Symposiaca* VI, 8).

Referring to the fact that ravenous hunger occurs after great fatigue, for instance after having walked through snow, and then disappears after partaking of only very small amounts of food, particularly a morsel of bread, one speaker contends that the heat being withdrawn from the interior and heaped up on the outside of the body, as for example the perspiration and the warm and tired hands and feet of the fatigued person, show, leaves inwardly a state of cold which causes a craving for food. Another says, no, the craving for food is not caused by the cold, but in the body something takes place similar to that which happens with metals in a very severe winter. There it is seen that cooling does not only cause congealing but also melting for in severe winters *ἀχφόναι μολίβδου* occasionally melt away, consequently something similar may be supposed to take place in the intestinal process, etc.

Probably, leaden grindstones are meant. (Plumbese cotes in WIJTTENBACH's translation, cueux de plomb in MONTAIGNE's).

4. According to a private communication from Dr. KRAUSE he has borrowed PLUTARCH's citation (see pag. 469) from a translation by KALTWASSER (Bd. 5, S. 594, Frankfurt a. M. 1793) where may be read:

Uebrigens ist es ausgemacht, dass die Kälte die Körper nicht nur verdichten, sondern sie auch zerschmelzen kann. In strengen Wintern geschieht es zuweilen, dass grosse Stücke Blei, womit die Bildsäulen an den Postamenten befestigt sind, zerschmolzen werden und herabfallen.

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[1]) Plutarchi chaeronensis varia scripta quae moralia vulgo vocantur. Lipsiae, ex officina Car. Tauchnitii 1820. Tomus IV, 339.

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Of this, however, nothing is to be found in PLUTARCH himself at the place mentioned.

5. Whilst ARISTOTLE makes a very clear distinction between κασσίτερος (tin) and μόλυβδος (lead) the question might be put whether PLUTARCH when using this last word really means what we understand by lead or whether we have also to think there of *tin*.

BERTHELOT says in his *Introduction à l'Etude de la Chimie des Anciens et du Moyen Age* [1]): "tout métal et alliage blanc, fusible et altérable au feu, s' appelait à l'origine *plomb*. Plus tard on distingua deux variétés: le plomb noir, qui comprenait notre plomb et plus rarement, notre antimoine, etc.; et le plomb blanc, qui comprenait notre étain et certain alliages de plomb et d'argent."

Of importance is also what BERTHELOT [2]) afterwards wrote in his "La Chimie au Moyen Age (1893) where he devotes a chapter to the names of *tin*.

"Le nom que κασσίτερος, employé dans HOMÈRE, (± 800 a. Chr.) paraît signifier un alliage de l'argent avec le plomb, peut être associé à l'étain: il n'a pris son sens actuel, dans toute sa précision, que vers le temps d'Alexandre (356—323 a. Chr.) et des Ptolémées... mais on s'exposerait à toutes sortes d'erreurs, en l'appliquant aux auteurs qui ont employé le même mot à des dates plus reculées."

We may, therefore, assume also in connection with the distinction made between κασσίτερος and μόλυβδος (see above), that in the time of ARISTOTLE (384—322 B. C.) the meaning of κασσίτερος corresponded with our idea of *tin* [3]).

It certainly seems worth while to study the behaviour of lead also at low temperatures.

Summarising, it appears from the above that there is reason to suppose that the changes which tin may undergo at low temperatures had already been observed at the time of ARISTOTLE, whilst nothing definite can, as yet, been said about an analogous conduct of lead.

Amsterdam, Chem. Lab. University, December 1900.

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[1]) Paris, 1889, p. 230—231.

[2]) Paris, Imprimerie nationale. Tome I, 367.

[3]) The statement that it also melts in water might make us again entertain a doubt.

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Physics. — Dr. G. BAKKER: "*Contribution to the theory of elastic substances.*"

If we leave electrical and magnetical forces out of consideration, the forces acting on a body are gravitation, external pressure or tension and the internal molecular pressure and thermic pressure. Though in the theory of elasticity the substance is substituted by a continuous agent and we have therefore strictly speaking not to deal with mutual action of molecules, I shall yet keep to the usual term, though the term cohesion seems more suitable to me than the term molecular pressure.

In the theory of elasticity, just as in the theory of capillarity, forces are assumed, which are only perceptible at exceedingly small distances. If these forces are supposed to have a potential, the potential function

$$-f\frac{e^{-qr}}{r}$$

which is a special case of the general function of Dr. C. NEUMANN,

$$\frac{Ae^{-\alpha r}}{r}+\frac{Be^{-\beta r}}{r}+\frac{Ce^{-\gamma r}}{r}+\ldots$$

might be of great use here, for if we take q very large, the forces between two volume-elements will rapidly decrease with the distance.

In his thermo-dynamical theory of capillarity VAN DER WAALS has found this potential function to be a probable function for the capillary forces. Afterwards I have further discussed this function in two papers, presented to the Academy the 28th of October and the 25th of November 1899, and I further applied it in my treatise "Zur Theorie der Kapillarität" (Zeitsch. für phys. Chemie XXXIII, 4. 1900).

Let us imagine an "infinitely small" volume-element in the body in consideration, and let us take that space as unity of volume. If U, B and ϑ are respectively the virial of the external forces, that of the molecular attraction and that of the thermic pressure, then the total virial per unity of volume is e.g.:

$$F=U+B+\vartheta \text{ [1]} \quad \ldots\ldots\ldots \quad (1)$$

[1]) The influence of gravitation is left out of consideration.

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I imagine the element to have the shape of a cube, the sides of which are parallel to the principal pressure-axes of the point in consideration, which I take as coordinate axes. Then the general expression for the virial:

$$F = -\Sigma \tfrac{1}{2}(Xx + Yy + Zz)$$

gives immediately:

$$U = \tfrac{1}{2}(p_1 + p_2 + p_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

p_1, p_2 and p_3 representing the principal pressures.

If S_1, S_2 and S_3 represent the molecular tensions in the same directions and θ the thermic pressure in the point in question, then:

$$p_1 = \theta - S_1, \quad p_2 = \theta - S_2 \quad \text{and} \quad p_3 = \theta - S_3$$

or

$$p_1 + p_2 + p_3 = 3\,\theta - (S_1 + S_2 + S_3).$$

So:

$$U = \frac{3}{2}\theta - \frac{1}{2}(S_1 + S_2 + S_3). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As the thermic pressure depends only on the condition of the substance in the immediate neighbourhood of the point [1]), where the value of the virial of the thermic pressure is θ [2]), we may take for θ also the value which this quantity would have if *at the same temperature* the substance round the point in consideration had the same density as in the point itself. If we take for the agent, which in these considerations is used as a substitute for the body which is thought to be isotropical, the potential function:

$$-f\frac{e^{-qr}}{r}$$

the following differential equation holds good for that agent:

$$\nabla_2 V = q^2 V + 4\pi f\varrho \text{ [3])}.$$

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[1]) In contrast to the molecular forces of attraction.

[2]) Zeitschrift für phys. Chemie XXXIII, 4 1900 p. 478.

[3]) Koninkl. Akad. v. Wetenschappen: Proc. Nov. 25th 1899 p. 2.

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For a region which is large enough and for which we think the density ϱ to be the same everywhere, $\nabla_2 V = 0$ and so:

$$V = -4\pi f \lambda^2 \varrho$$

or substituting a for $2\pi f\lambda^2$: $\left(\lambda = \frac{1}{\varrho}\right)$

$$V = -2a\varrho$$

the tension S now becoming:

$$S = \frac{V^2}{4\pi f \lambda^2} = a\varrho^2 \text{ [1)]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If in this case we call the pressure p, then:

$$p = \theta - a\varrho^2 \text{ [2)]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

p is the pressure of the homogeneous phase with the density ϱ of the point in question and at the temperature of that point.

From (5) follows:

$$\frac{3}{2} p v = \frac{3}{2} \theta v - \frac{3}{2} a \varrho \quad (v = \text{specific volume}) \quad . \quad . \quad . \quad (6)$$

If F_1 is the virial of the homogeneous mass per unity of mass, then:

$$F_1 = \frac{3}{2} p v + \frac{3}{2} a \varrho + \vartheta_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

for, as may be easily shown, the virial is $\frac{3}{2} \times$ the potential energy with reversed sign. (See Zeitschrift für phys. Chemie XXI. 3. 1896,

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[1)] Konink. Akad. v. Wetenschappen: Proc. Nov. 25th 1899 p. 219 and 330.

[2)] If the expression $\theta = \frac{RT}{v - b}$ held for the thermic pressure for an isotropical substance with a certain density, we should get the same equation of state as that of VAN DER WAALS' for gases and liquids.

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pag. 503). Further $\frac{3}{2} p v$ is the virial of the external forces and ϑ_1 that of the thermic pressure (per unity of mass).

If we substitute in (7) the value for $\frac{3}{2} pv$ derived from (6) we get:

$$F_1 = \frac{3}{2} \theta v + \vartheta_1 .$$

If we suppose that the total virial of the mass-unity is a pure function of the temperature, just as for liquids and gases, and further that ϑ_1 depends only on the density (and temperature) then:

$$F_1 \varrho = F \text{ and } \vartheta_1 \varrho = \vartheta$$

and so according to (1):

$$U + B + \vartheta = \frac{3}{2} \theta + \vartheta$$

By substitution in (3):

$$B = \frac{1}{2} (S_1 + S_2 + S_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or in words:

the virial of the molecular forces per unity of volume is half the sum of the three principal tensions.

If we put $A = -f$ and $B = 0$ in the expressions which in the paper already mentioned I found for the tensions p_{xx}, p_{yy} and p_{zz} (pag. 318), through which the potential function

$$\frac{Ae^{-qr} + Be^{qr}}{r} \quad \text{becomes} \quad -f\frac{e^{-qr}}{r}$$

we get:

$$-8\pi f p_{xx} = \left(\frac{dV}{dx}\right)^2 - \left(\frac{dV}{dy}\right)^2 - \left(\frac{dV}{dz}\right)^2 - q^2 V$$

$$-8\pi f p_{yy} = \left(\frac{dV}{dy}\right)^2 - \left(\frac{dV}{dz}\right)^2 - \left(\frac{dV}{dx}\right)^2 - q^2 V$$

$$-8\pi f p_{zz} = \left(\frac{dV}{dz}\right)^2 - \left(\frac{dV}{dx}\right)^2 - \left(\frac{dV}{dy}\right)^2 - q^2 V$$

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By addition:

$$-8\pi f(p_{xx}+p_{yy}+p_{zz}) = -\left\{\left(\frac{dV}{dx}\right)^2+\left(\frac{dV}{dy}\right)^2+\left(\frac{dV}{dz}\right)^2\right\}-3q^2V$$

The sum of the tensions $p_{xx}+p_{yy}+p_{zz}$ is therefore independent of the direction of the sides of the cube-shaped element in consideration. We may therefore represent the sum by $S_1+S_2+S_3$ and find then:

$$B=\frac{R^2}{16\pi f}+\frac{3V^2}{16\pi f\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad (9)\left(\lambda=\frac{1}{q}\right)$$

The tensions S_2 and S_3 normal to the lines of force appeared to be the same. We found for them:

$$S_2=S_3=\frac{R^2}{8\pi f}+\frac{V^2}{8\pi f\lambda^2}$$

and

$$S_1=\frac{R^2}{8\pi f}-\frac{V^2}{8\pi f\lambda^2}$$

while we found for the potential energy per unity of volume:

$$W=-\frac{R^2}{8\pi f}-\frac{V^2}{8\pi f\lambda^2}.$$

Now we can easily derive the relation:

$$S_2-S_1=-3W-2B \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or in words:

The difference of the tensions normal to and in the direction of the lines of force (per unity of surface) *is three times the work required to rarefy the substance infinitely, diminished with twice the virial of the molecular forces of attraction* (per unity of volume).

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Dilatation.

If λ and μ are two constants, we have according to KIRCHHOFF for the projections of the displacements of a point, whose coordinates are x, y and z:

$$(\lambda + 2\mu)\frac{\partial u}{\partial x} + \lambda\frac{\partial v}{\partial y} + \lambda\frac{\partial w}{\partial z} = -X_x \quad \begin{matrix}(-X_x \text{ is there-}\\ \text{fore a tension)}\end{matrix}$$

$$\lambda\frac{\partial u}{\partial x} + (\lambda + 2\mu)\frac{\partial v}{\partial y} + \lambda\frac{\partial w}{\partial z} = -Y_y$$

$$\lambda\frac{\partial u}{\partial x} + \lambda\frac{\partial v}{\partial y} + (\lambda + 2\mu)\frac{\partial w}{\partial z} = -Z_z$$

By composition:

$$(3\lambda + 2\mu)\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) = -(X_x + Y_y + Z_z).$$

The second factor in the left-side member represents the dilatation, and is generally indicated by the symbol ∇. Therefore:

$$\nabla = -\frac{X_x + Y_y + Z_z}{3\lambda + 2\mu} \quad \ldots\ldots \quad (11)$$

The quantities X_x, Y_y and Z_z correspond to the quantity which we should call the hydrostatic pressure in case of a liquid. If therefore the molecular tensions are represented by S_{xx} etc., we have:

$$X_x = \theta - S_{xx}$$

$$Y_y = \theta - S_{yy}$$

$$Z_z = \theta - S_{zz}$$

By substitution of θ from (3)

$$X_x + Y_y + Z_z = 3\theta - (S_{xx} + S_{yy} + S_{zz}) = 3\theta - (S_1 + S_2 + S_3) = 2U$$

or according to (11)

$$\nabla = -\frac{2U}{3\lambda + 2\mu} \quad \ldots\ldots \quad (12)$$

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Applications.

1. *Elongation of a prism.* We imagine at the two ends a force S per unity of surface in the direction of the longitudinal axis. If we apply formula (12) to every volume-element of the prism, the total increase of volume becomes:

$$\int \nabla \, d\tau = -\frac{2\int U \, d\tau}{3\lambda + 2\mu}.$$

For space-elements which are quite inclosed by others, the increase of volume for the external virial (external with regard to such an element) is neutralized by that of the surrounding ones and finally the total external virial is that of the external forces acting on the prism. That virial is in this case: $-\frac{1}{2} S l d$.

Therefore:

$$\int \nabla \, d\tau = -\frac{2\,U}{3\lambda + 2\mu} = \frac{S l d}{3\lambda + 2\mu} \qquad (d = \text{section}).$$

The dilatation is therefore:

$$\frac{S}{3\lambda + 2\mu}$$

2. *Dilatation of a hollow cylinder.* Let S be the corresponding force just mentioned, P and p the forces per unity of surface, normal to the outer and inner surface, taken positively in the direction of the radius, then, if l represents the length, r and R the radii internal and external, the virial of S is:

$$-\tfrac{1}{2} S l (\pi R^2 - \pi r^2),$$

the virial of P:

$$-\tfrac{1}{2} \Sigma P R = -\tfrac{1}{2} R \times 2\pi R l P$$

and that of p:

$$-\tfrac{1}{2} r \times 2\pi r l p.$$

Therefore:

$$-2\,U = S l \pi (R^2 - r^2) + 2\pi l (P R^2 + p r^2).$$

The total increase of volume divided by the volume $\pi (R^2 - r^2) l$ yields for the dilatation:

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$$\nabla = \frac{1}{3\lambda + 2\mu}\left\{S + 2\frac{P R^2 + p r^2}{R^2 - r^2}\right\}$$

3. *Dilatation of a spherical shell.*

Let p be the internal, P the external pressure, both calculated positively in the direction of the radii r and R, then is, according to the general expression of the external virial $-\frac{3}{2}pv$, the virial of p:

$$-\frac{3}{2}p \times \frac{4}{3}\pi r^3 \text{ and of } p: -\frac{3}{2}P \times \frac{4}{3}\pi R^3.$$

After having divided by $3\lambda + 2\mu$ and by the original volume $\frac{4}{3}\pi(R^3 - r^3)$, we get for the dilatation:

$$\nabla = -\frac{2U}{3\lambda + 2\mu} : \frac{4}{3}\pi(R^3 - r^3) = \frac{3}{3\lambda + 2\mu}\frac{PR^3 + pr^3}{R^3 - r^3}$$

4. OERSTED's *Piëzometer.*

If V is the external and v the internal volume, then the virial of the external pressure is $p : \frac{3}{2}pV$ and that of the internal pressure: $-\frac{3}{2}pv$. As the original volume of the substance forming the shell is $V - v$, the dilatation becomes:

$$\nabla = -\frac{1}{3\lambda + 2\mu}\frac{2 \times \frac{3}{2}(V - v)}{V - v} = -\frac{3p}{3\lambda + 2\mu}$$

So we see that the value of the ratio ∇ does not depend on the external or internal volume nor on the form. The external volume is therefore compressed in a proportion as if the vessel were massive, which corresponds with the views of COLLADON and STURM and is opposed to those of OERSTED.

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Physics. — J. C. SCHALKWIJK: "*Precise isothermals. I. Measurements and calculations on the corrections of the mercury meniscus with standard gas-manometers*" *(Continued.)* (Communication N°. 67 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

§ 6. We now can change the formulae found so, that they represent the surface of interpolation meant in § 3 for the mean height up to the limits $R = 0$ and $\delta = 0$.

For the narrow tubes we find then:

$$f = \frac{1}{2}\delta R + \frac{1}{6}\delta^3 R + \frac{1}{96}\frac{s}{H}\delta R^3 (1+\delta^2)^3 \quad . \quad . \quad . \quad (I)$$

and for small values of δ:

$$f = \delta R \left\{ 1 - \frac{\Sigma \frac{1}{(n!)^2 (n+1)} \left(\frac{s}{4H} R^2\right)^{n-1}}{\Sigma \frac{1}{(n!)^2} \left(\frac{s}{4H} R^2\right)^{n-1}} \right\} \quad . \quad . \quad . \quad (II)$$

It should be noted that in both the expressions the factor of δR is greater than $\frac{1}{2}$.

In order to be able to calculate f in the limiting cases by means of these formulae, we must introduce the value of $\frac{s}{H}$. This is not exactly known to us. Fortunately an uncertainty in $\frac{s}{H}$ is of little interest for the correspondence meant in § 4, since for small values of R, $\frac{s}{H}$ in the formula (I) occurs only in that term in which also R^3 appears, so that a change in $\frac{s}{H}$ has only little influence on f. In the same way in small values of δ the influence of a change in the value of $\frac{s}{H}$ is unimportant for values of R smaller than 0,045 cm.

In order to demonstrate this I have calculated for $\delta = 0{,}05$ two menisci, for which I have not accepted $\frac{H}{s} = 0{,}0354$ cm^2, which number may be derived from the data of QUINCKE for mercury,

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three hours after the formation of a drop[1]), but 0,0433 cm². for mercury, immediately after the formation of the drop. Then we have for:

$$R = 0{,}588 \text{ cm.} \quad f = 0{,}0168,$$

$$R = 0{,}455^5 \text{ »} \quad f = 0{,}0125;$$

while for $\frac{H}{s} = 0{,}0354$ cm². we get for:

$$R = 0{,}588 \text{ cm.} \quad f = 0{,}0172,$$

$$R = 0{,}455^5 \text{ »} \quad f = 0{,}0127.$$

And so we may easily complete the direct measurements by the limiting cases calculated on the supposition $\frac{H}{s} = 0{,}0354$ cm². up to the surface of interpolation. From § 7 it will appear that this value may certainly be put in stead of that which existed with the menisci observed by us.

I will now first draw the curve which represents f as a function of δ with the tube of 0,283 cm. radius (curve I in fig. VI of the plate)[2]).

For this I have drawn δ from the point A in a horizontal direction for which 0,0025 = 1 mm. is taken and f in a vertical direction for which 0,0005 = 1 mm.

In this manner from the menisci measured the points B, C, D and E have been obtained; but here it must be borne in mind that the curve is not determined by these points themselves, but by the condition that B and E and in the same way C and D must always be situated at equal distances on either side (comp. §§ 2 and 3).

Further are computed by means of the yet unsimplified formula:

$$f = \delta R - \sum \frac{\alpha_n}{n+1} R^{2n}$$

---

[1]) But even this number is far from being certain, for from two kinds of series of experiments at 20° C., QUINCKE found also values corresponding to $\frac{H}{s} = 0{,}0391$ and $\frac{H}{s} = 0{,}0396$ cm².

[2]) Given in the Proceedings Dec. 1900.

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the following values:

$\delta = 0{,}0991$; $f = 0{,}0148$ represented by the point F;

$\delta = 0{,}0708$; $f = 0{,}0105$ » » » » G;

$\delta = 0{,}0425$; $f = 0{,}00627$ » » » » H.

And then the line I is drawn.

In the same way line II in fig. VI is obtained for the tube of 0,382 cm. radius. From the point A, δ and f have been drawn in a similar manner and so we get the points L, M, N and O, for which the paired points are again L and N, together with M and O. The points P and Q have again been calculated.

Line III in the same fig. VI applies to the tube of 0,5814 cm. radius, and has been drawn from the point A. Here the paired points are S and T, and also U and V; W and X have been calculated. The points S' and T' as well as U' and V' belong to measurements in a tube of about the same width. It is difficult to draw the line through W and X and also between the paired points. But as I do not use tubes of more than 0,4 cm. radius, I have not considered this much further, because in such wide tubes the rim is no longer perfectly circular and parallax can not easily be avoided in the measurements.

Then fig. IV is drawn in which f as a function of R has always been drawn for the same value of δ. The scale values are again for f: $0{,}0005 = 1$ mm. and for R: $0{,}0025 = 1$ mm.

First we have drawn the points with $R = 0{,}2832$ cm. in the line I for the values of δ: 0,05; 0,1; 0,15; 0,2; 0,25; 0,3; 0,35; 0,4; the straight line on which these points are situated is in fig. IV also numbered by *1*.

Secondly the points with $R = 0{,}382$ cm. in the line II for the same values of δ; the straight line is also marked *2*.

Then the points for $R = 0{,}04$ cm. and $R = 0{,}1$ cm. have been calculated and lastly a number of points are calculated according to the formula (II), all for $\delta = 0{,}05$.

The points Y and Z are those calculated with the value $\frac{H}{s} = 0{,}0433$ cm^2.

Now the line for $\delta = 0{,}05$ could be drawn, by which the type for the lines $\delta =$ constant is known. Moreover we could draw each time the beginnings of those lines at small value of R, and so they

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could be continued through the points given by the lines *1* and *2*.

The rest of fig. VI has been derived from fig. IV by seeking each time for the same value of R in fig. IV the corresponding values of δ and f, and by drawing them anew as in the case of the curves I, II and III in fig. VI.

Curve V in fig. VI belongs to the tube of 0,409 cm. radius, of which only one meniscus was measured. The remaining lines in fig. VI belong to 0,05; 0,1; 0,15; 0,2; 0,25; 0,3; 0,35; and 0,4 cm. radius.

§ 7. The form of the meridian section of the meniscus can, if $\frac{H}{s}$ were exactly known, also be found graphically in the way shown by Lord KELVIN [1]). For if ϱ is the radius of curvature at the top of the meniscus, r_1 the radius of curvature at the point P of the normal section perpendicular to the meridian plane and r_2 the radius of curvature in the meridian plane, then we can write the equation:

$$\frac{1}{r_2} = \frac{s}{H} h + \frac{2}{\varrho} - \frac{1}{r_1},$$

so that, if we start from the top with a given radius of curvature we can always calculate r_2 if we have accepted some value for for $\frac{s}{H}$. For this I have again taken the value 28,25, hence $\frac{H}{s} = 0{,}0354$ cm^2. and then all the values must be expressed in cm. And so fig. VIII has been drawn on a 10 times magnified scale, in which $\varrho = 0{,}8$ cm. has been taken [2]). For r_1 and h we have each time taken the values which they have at the starting point of each element of the meridian curve so that the curvature is sure to be too small. In the same way fig. IX has been drawn in which h has been taken, as it is at the end of each element, so that the curvature is too large.

---

[1]) To a request to Prof. PERRY about the drawings of the menisci made after this method, Prof. PERRY answered that they were not published in the paper in the Transactions of the Royal Society of Edinburgh and were afterwards lost.

[2]) This drawing, as well as fig. IX was originally constructed on a 30 times magnified scale and the curve was not divided into four as in the figure, but in twenty-four elements; in the reproduction on a $\frac{1}{3}$ scale only four lines of construction have been drawn.

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The two curves are combined in fig. X on the original 30 times magnified scale and there the mean curve has been drawn as a probable meridian section. Fig. XI represents the meniscus when the radius of curvature is 1,1 cm. at the top; it was drawn on a 25 times magnified scale, but is here again reproduced with some construction lines on a $^{25}/_{3}$ scale; while for h we have here always taken the height of the middle of each curve element and in the same way for r_1 the value, which that radius of curvature would have in the middle.

From the original drawings of the figures X and XI I have again calculated for several values of R (the radius of the tube), the height and the volume of the meniscus and from them again δ and f and I have also indicated these values in fig. VI by little squares; the deviation from the curves drawn already remains below the limit we require. The following values are found:

R.	p.	δ.	I.	f.	in fig. VI indicated by:
0,2	0,03	0,15	$\pi \times 0{,}000619$	0,0155	β
0,25	0,0487	0,195	$\pi \times 0{,}001582$	0,0253	γ
0,2832 (I)	0,0653	0,230	$\pi \times 0{,}00278$	0,0346	δ
»	0,0424	0,150	$\pi \times 0{,}00180$	0,0225	η
0,3	0,0758	0,253	$\pi \times 0{,}00367$	0,0408	ε
»	0,0493	0,164	$\pi \times 0{,}00238$	0,0264	θ
0,35	0,115	0,329	$\pi \times 0{,}00786$	0,0642	ζ
»	0,0727	0,208	$\pi \times 0{,}00484$	0,0395	ι
0,382 (II)	0,092	0,241	$\pi \times 0{,}00748$	0,0513	$\varkappa$
0,4	0,105	0,262	$\pi \times 0{,}00976$	0,0610	λ

§ 8. It follows from the given dimensions for menisci derived from the value $\frac{H}{s} = 0{,}0354$ cm^2. that the difference in value which $\frac{H}{s}$ has had in the menisci which I measured directly cannot have had much influence on the determination of the volume.

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The mercury in the tubes used for that determination of the volume of the menisci was treated in exactly the same way as for the calibration of my piezometer tubes. And so we have as much certainty as can be obtained, that the values derived from the direct measurements of the menisci are applicable to the menisci which occur in the calibration.

Also for values of $\frac{H}{s}$ not deviating much from 0,0354 cm²., as they may occur perhaps, when the piezometertubes are used with compressed gas, it will be allowable to use the values for the menisci which we have now found.

In general it is obvious that from the differential equation for h and r the same relation will be found when the unit of length is changed in the ratio of the square root of $\frac{H}{s}$. Thereby δ remains unchanged. If therefore $\frac{H}{s}$ changes from 0,0354 to 0,0433 cm²., in order to be able to use the same values the unit of length must be taken $\sqrt{1,225}$ or 1,107 times larger. If for instance we desire to know f for $\delta = 0,35$ and $R = 0,3$ cm., $\frac{H}{s} = 0,0433$ cm². then we must look for it at $\delta = 0,35$ and $R = 0,271$ cm.; we then find $f = 0,0506$ and the value desired is 0,0560, while we find from the values measured: 0,0566; which would give a deviation of about 1 percent, and so within the limits we have indicated. For wider tubes the deviation increases; if for instance we want to know f for $\delta = 0,35$ and $R = 0,4$ cm., $\frac{H}{s} = 0,0433$ cm²., then we find in Fig. IV at $\delta = 0,35$ and $R = 0,361$ cm., by continuing the curve a little $f = 0,0735$ and so the value sought is 0,0814; while from Fig. VI 0,0904 follows for the value measured, a large difference, for which it should be borne in mind that these numbers have not the accuracy of the values at a smaller δ, because they are obtained by continuing the curves for $R = \text{const.}$ and $\delta = \text{const.}$ a little beyond the range of observation. From the two instances given it appears that when H increases, for wide tubes (R=0,4 cm.), the mean height decreases perceptibly. From the situation of the points ζ, $\varkappa$ and λ it would then follow that in the experiments $\frac{H}{s}$ would have been just a little smaller than 0,0354 cm². While as we see our results can be applied with a great certainty for the

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calibration, when we use compressed gas, this is dependent on the question how $\frac{H}{s}$ or as we must write that factor then: $\frac{H_{1,2}}{s_1 - s_2}$ varies with the pressure of the gas. Corresponding to the important changes of $\frac{H}{s}$ arising from contact of the mercury surface with the air, the contact with a highly compressed gas can also influence it. As I could not obtain any indications on this point, I have assumed in my calculations that the influence of the pressure on $\frac{H_{1,2}}{s_1 - s_2}$ may be neglected; it may be that later on we will be able to apply these corrections again.

That however these corrections will not probably become important for my determinations of isothermals, follows from the fact that the wide tube has only been used to 8 atm. for which the change of $\frac{H}{s}$ by the pressure will certainly be only very small; while at high pressures the volume is measured in narrower tubes, and we have proved that the influence of $\frac{H}{s}$ decreases as the tube becomes narrower.

§ 9. Although my research on the volume of the mercury meniscus has been made in order to evaluate the correction in the calibrations of our piezometertubes and in the measurements made by means of them, I have with a view to possible researches, for which the meniscus must be known still more accurately, read the *values of f* as accurately as possible in the figures IV and VI on the original drawing of which the scale was twice and a half as large again as that for the plate. We can now combine the values obtained in the following table; those which deviate imperceptibly from the mean height of the segment of a sphere have been printed in a small type.

To make it prominent for which menisci the deviation from a segment of a sphere begins to become important in our accurate determination of isothermals I have underlined them in the table [1]). The values obtained by extrapolation are in italics.

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[1]) In the calibration of the piëzometertube of 0.4 cm. 15 menisci occurred, the heights of which varied from 0.087 ($\delta = 0.22$) cm. to 0.143 ($\delta = 0.36$) cm., mean height 0.114 ($\delta = 0.28^5$) cm.; in the measurements 80 menisci occurred from 0.092 ($\delta = 0,23$) cm. to 0.144 ($\delta = 0.36$) cm. height; most of them between 0.108 ($\delta = 0.27$) and 0.127

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	δ							
R in c.m	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
0.05	0.0012[6]	0.0025[2]	0.0038	0.0050[6]	0.00637	0.00773	0.0091	0.0107
0.1	0.0025[2]	0.0050[4]	0.0076	0.0102	0.0128	0.0155	0.0183	0.0213
0.15	0.0037[6]	0.0075[6]	0.0114[5]	0.0153	0.0192[5]	0.0232[5]	0.0274	0.0318
0.2	0.0050[5]	0.0103	0.0155	0.0206	0.0257	0.0310	0.0366	0.0426
0.25	0.0065[5]	0.0131	0.0196[5]	0.0261[5]	0.0327	0.0393	0.0462	0.0536
0.3	0.0080	0.0159	0.0239	0.0320	0.0401	0.0483	0.0566	0.0657
0.35	0.0093[5]	0.0188	0.0283	0.0384	0.0489	0.0592	0.0700	*0.0815*
0.4	0.0108[5]	0.0218	0.0331	0.0453	0.0583	0.0737	*0.0904*	

I thought it better to let the table stand in this form, because on account of the slight curvature of the lines in fig. IV and VI a better interpolation is possible than if I had expressed the volume, in terms of the height and the radius.

But if many menisci at one width of the tube must be calculated, then tables must be derived for them from the preceding table.

If finally we reconsider the numerical example of § 1 we calculate from this table a section of 0,5 cm.^{2} and a height of 0,14 cm., a volume of 0,045 cc., while the segment of a sphere gives 0,0365 cc., and so we find a difference of about 0,0085 cc. or 23 percent, or more than 7 times the error allowed in our measurements, so that the correction calculated in these communications is indispensable for the accurate measurements aimed at.

($\delta = 0.32$) cm., on an average 0.115 ($\delta = 0.29$) cm. For the tube of 0.283 cm. radius I obtained in the calibration 16 menisci from $p = 0.042$ ($\delta = 0.15$) to $p = 0.095$ ($\delta = 0.33^5$) cm., on an average $p = 0.073$ ($\delta = 0.258$) cm.; in the measurements 33 menisci from $p = 0.031$ ($\delta = 0.11$) to $p = 0.121$ ($\delta = 0.43$) cm., on an average $p = 0.075$ ($\delta = 0.265$) cm. The third and the fourth tube are sufficiently narrow, so that we can omit the correction on the segment of sphere.

(February 20, 1901.)

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday February 23, 1901.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 23 Februari 1901 Dl. IX).

CONTENTS: Prof. F. A. F. C. WENT: "On the Influence of Nutrition on the Secretion of Enzymes by Monilia sitophila (Mont.) Sacc." p. 489. — Dr. A. SMITS: "Determination of the decrease of vapour-tension of a solution of Na Cl at higher temperatures", (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 503. — Dr. A. SMITS: "Some observations on the results obtained in the determination of the decrease in vapour-tension and of the lowering of the freezing point of solutions, which are not very dilute", (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 507. — Prof. J. D. VAN DER WAALS: "The equation of state and the theory of cyclic motion", p. 515. — Prof. H. G. VAN DE SANDE BAKHUYZEN: "Report of the Committee for the organization of the observations of the solar eclipse on May 18th 1901", p. 529.

The following papers were read:

Botanics. — Prof. F. A. F. C. WENT: "*On the Influence of Nutrition on the Secretion of Enzymes by Monilia sitophila (Mont.) Sacc.*".

(Read January 26, 1901).

The mould Monilia sitophila is used in the West of Java to cause decomposition in cakes of Arachis seeds; these are then eaten by the Sundanese under the name of *onchom*.

Spontaneously this mould occurs on putrefying bread and wheat-flour and has also been found in France; in Java I met with this Monilia growing spontaneously on dead leaf-sheaths of the sugar-cane in the residency of Pekalongan (where onchom cakes are

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unknown). Material for investigation I received by the interference of Dr. A. G. VORDERMAN, whilst the determination was done with the kind help of Prof. C. A. J. A. OUDEMANS.

Like other Monilia species this mould possesses a branched mycelium from which arise the conidia-bearing hyphae up in the air; these are strongly ramified and are often for the greater portion of their length built up of chains of conidia, which are elliptically shaped, much varying in size (from 5 to 14 μ diam.); they separate very easily, after having for a time been united by a connecting part. In rich cultures the hyphae are often united into tree-shaped masses, whilst the walls of the culture vessels are mostly coated with fringelike, downward pending, loose conidia-bearing filaments. I found that the presence of a moist atmosphere is a condition for the appearance of conidia; hence, their formation can be almost totally suppressed by keeping the air above the cultures as dry as possible, especially when the nutrient liquid is much concentrated.

Probably the fungus has yet another form of reproduction; at least I repeatedly found characteristically wound hyphae, which gave the impression of young perithecia. I did not however succeed in bringing them to further development, however much I varied the culture conditions (neither, for instance, when suddenly introducing a strongly fed mycelium into water, which has in some cases been successfully applied by KLEBS [1]).

Pigment.

Monilia sitophila is a most striking mould by its bright orange-red colour. The pigment can be solved in absolute alcohol, ether, benzol, chloroform, etc. by which a solution is obtained of gold-yellow to brown-red with a faintly green fluorescence; after evaporation of the solvent, brown, fatty drops remain; insoluble is the pigment, inter alia in water, acetic acid and hydrochloric acid. The absorption spectrum of the pigment-solution shows a dark zone, embracing the whole of the blue and violet portion of the spectrum, from about *F*.

Under the microscope the protoplasts often give the impression of being coloured uniformly orange, but the pigment is also seen lying in drops in the protoplasm. I suppose that this is always the case, but that these drops are often so small that they cannot be distinguished separately.

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[1]) Jahrb. für wiss. Botanik 33. 1899, p. 513.

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The mould has the remarkable property of exclusively forming this pigment when exposed to the light. If Monilia sitophila is grown in the dark, the mycelium and the conidia remain colourless; if however such a culture is placed in diffuse day-light, a light rosy tint sets in after 2 to 3 hours, which slowly passes into orange. Exposure to the light during only 15 minutes is sufficient to bring about a faintly rosy tint after a few hours, which however does not pass into orange in this case. A still shorter exposure to light seemed to cause a slight change of colour, if the action however was shorter than 5 minutes, the mycelium remained white.

It was furthermore proved that the blue and violet rays (the same which are absorbed by the pigment) are those which exert the above influence. If the mould is grown in the light, which has passed either through a kalium-bichromate solution or through a solution of the pigment itself, the mycelium continues colourless, whilst a bright orange-yellow tint appears when the culture is lighted by rays that have passed through a solution of cuprammoniumoxide.

The signification of this pigment production for the life of the plant is not yet clear to me; perhaps it protects the enzymes, produced by the mould, against the influence of the light; it is my intention to make a further investigation of this point.

Very frequently the medium on which the mould is grown, takes a brown colour, especially in old cultures. This stands in no relation whatever to the influence of the light, but, on the contrary, depends on the chemical composition of the nutrient medium. This brown colour, namely, appears only then, when the medium contains albuminous matter, peptones, or tyrosin, so that this is probably due to a secretion of tyrosinase.

Conditions of Nutrition.

Monilia sitophila thrives very well on number of natural media, such as Arachis seeds, bread, carrots, milk, broth, infusions of plums or raisins, somewhat less on the white of eggs, potatoes or sliced apples.

The use of media of exactly known composition proves that albuminous substances and peptone can serve as sources, both of carbon and nitrogen for our mould, whence the value of suchlike substances, as nitrogen food alone, is difficult to determine. Excluding these, one of the best sources of nitrogen (glucose being given as carbon nutrient), proves to be tyrosin, further asparagin, asparagin

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acid, leucin, anorganic nitrates, ammonium salts and nitrites, lastly, alanin and glycocol. Bad sources of nitrogen are urea and hippuric acid, whilst kreatin and coffeïn can still less serve as such. Many of the here mentioned organic compounds can serve as carbon food too, though mostly no vigorous mycelium is formed in this case.

As sources of carbon stand foremost, besides the already mentioned albuminous matters and peptones, the carbohydrates.

Of the substances examined, we must first of all mention raffinose, whilst also the following ones can be quite well utilised as sources of carbon: starch, dextrin, maltose and cellulose, in less degree glucose, fructose, mannose and glycogen, lastly cane-sugar, galactose, lactose, arabinose, arabin and inulin. Aromatic compounds seem unfit to serve as sources of nitrogen; on the other hand several non-carbohydrates of the fat-series may serve as such: among the alcohols in the first place glycerin, further mannite, erythrite, dulcite and in very small degree ethylalcohol; of the acids (in the form of salts) may be mentioned acetic acid, tartaric acid, lactic acid, malic acid, finally also acid-amids and amidoacids, such as asparagin, asparagin acid and glycocol. Fats are bad sources of carbon, yet the mould succeeds in getting some nourishment out of them.

Although in this short paper I will not enter into ampler details concerning the conditions of nutrition, a few points are worth special mention. The optimum temperature for the development of Monilia sitophila lies at about 30° C.; at this temperature several substances can still be used as nutrients, which at ± 15° C. are valueless as such. Hence, if the object is to grow the mould at the ordinary room temperature, this will only succeed when the conditions of nutrition are well chosen, but even then, the development goes on rather slowly.

Furthermore it should be observed that the value of a nitrogen food depends on the carbon food present, and the reverse. If for instance, maltose, glucose, lactose, cane-sugar and glycerin are offered as sources of carbon, then maltose proves to afford the most vigorous development when tyrosin, glycocol, hippuric acid, kreatin, or leucin serve as source of nitrogen, whilst cane-sugar is the best source of carbon with asparagin as source of nitrogen, and finally, when alanin is used, the development at the nutrition with glycerin is three times more vigorous than with any of the other examined substances. It appears to me that the explanation of this phenomenon should perhaps be sought in the greater or smaller facility with which the plant can form proteids from the carbon and

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nitrogen food which it receives. For we know from experiments with higher plants by HANSTEEN [1]), that Lemna can form proteids from asparagin and glucose, but not from asparagin and cane-sugar; on the other hand, it can form them from cane-sugar and glycocol, but not from glucose and glycocol.

Lastly, in such experiments distinction should be made between the value of a carbon food as plastic material for the production of the constituents of the plant-body and as respiration material. It seems to me that this is most evident when comparing the result of nutrition with glycerin alone, raffinose alone, and with both combined. If as food is used 100 cm. of a liquid which contains, besides 0.5 pCt. NH_4NO_3, and the other required anorganic salts 3.27 pCt. glycerin, then after about two weeks, a crop is obtained of $\pm$ 25 mgrs. (expressed in dry matter of the mould). If instead of glycerin 0.16 pCt. raffinose is taken, the crop is under the same circumstances about 19 mgrs.; if however these two are combined, so that the nutrient liquid contains 0,16 pCt. raffinose and 3.24 pCt. glycerin then the crop is 150 mgrs. In order to get an equal crop with raffinose as the only carbon food, 2,5 pCt. of this substance must be added to the nutrient liquid, whilst with glycerin such a crop is not to be obtained. This can be explained when we admit that glycerin is not a fit material for the production of protoplasm or cell-wall (at least with NH_4NO_3 as source of nitrogen), but is, on the other hand a good respiration material.

As well on an acid as on an alkaline medium the mould can grow; to 100 cm. of nutrient liquid can be added 10 cm. of $^1/_{10}$ norm. sulphuric acid, even 25 ccm. of $^1/_{10}$ norm. caustic potash, and yet development will take place.

The mould can live anaerobiontically; as well in BUCHNER's tubes, where the oxygen is absorbed by pyrogallol and caustic soda, as in a current of hydrogen, a rather vigorous development is obtained, though less than in the air. It seems to me that the development decreases, when the last traces of free oxygen are better removed, so that in complete absence of this element the development is probably quite stopped. In an atmosphere of hydrogen, CO_2 is developed and alcohol is formed.

Decompositions caused by Monilia sitophila.

Fats as well as proteids and carbohydrates are liable to certain

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[1]) Jahrb. für wiss. Botanik. 33, 1899, p. 117.

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decompositions when introduced into a culture fluid in which Monilia sitophila is present.

Fats are, although very slowly, splitted up into glycerin and free fatty acids. Probably the mould uses the glycerin as food. This can be easily demonstrated by growing Monilia sitophila in a fluid which contains as carbon food butter-fat or Arachis-oil or another fat and to which is added a little litmus. The development of the mould takes place very slowly and at the same time the solution is seen to grow more and more red; in the absence of fats the mould forms no acid. This decomposition is probably caused by a secreted enzyme, a lipase. If the mould grows on milk, this becomes acid, and at the same time the casein precipitates, which in my opinion, should be attributed to the decomposition of the fats of the milk. Hence, when milk, rendered free from fat by filtration, is used as medium for our Monilia, no precipitate appears but on the contrary, the slight deposit which forms at sterilisation, is gradually solved. This is a consequence of the secretion of a proteolytic enzyme, to which I shall presently return. The dark brown colour which these liquids thereby assume, is, as mentioned above, a consequence of the presence of proteids.

Nutrient gelatin is liquefied by the mould, as well in neutral, as in alkaline or feebly acid condition, in absence and in presence of free oxygen. So it was obvious that a proteolytic, more particularly, a tryptic enzyme, is secreted. If a culture is made in a peptone solution, filtered after some time, and introduced into tubes of coagulated gelatin (with addition of an antisepticum, such as toluene or thymol), then the gelatin at the surface is slowly liquefied, this does not occur when the said liquid has first been boiled; hence it is evident that a gelatin-liquefying enzyme was secreted by the mould. The quantity of this enzyme is however very small which renders its examination troublesome. Moreover the secretion proves to depend on the nutrition of the mould; it is, e.g., found when peptone is given as food, not when glycogen and NH_4NO_3 are the nutrients. I did not, however, pay much attention to this fact as something similar is much more distinctly observed with the carbohydrates and can there be better measured.

The splitting of the proteids goes certainly further than the appearance of peptones, so it is easy to state the formation of NH_3. It is also evident from the following experiment, that peptone is decomposed by the enzyme (or enzymes) in question here: When from a peptone liquid the mould is filtered and the liquid is allowed to stand with a little toluene, the rotation to the left which is a

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consequence of the presence of peptone slowly decreases. This change of rotation does not occur when the liquid has first for a short time been heated to 100° C. The decomposition products of proteids are however also found in cultures to which no trace of any proteid has been added, e.g. in glycerin and KNO_3 solution. These can here have only taken origin from the protoplasm of already dead cells of the mould.

I have given much attention to the action exerted by Monilia sitophila on carbohydrates. Starch, dextrin, cane-sugar and maltose are hydrolised by the mould, lactose is not changed, although, as said above, it can serve as food. Cellulose is attacked and converted into a reducing sugar, which is however evidently soon consumed as food, so that only a feeble reduction of FEHLING is observed in culture liquids where cellulose is present as carbon food. That the cellulose is attacked is easily seen under the microscope, when the mould is grown on Arachis seeds, the cell-walls are in all directions infested by the hyphae and so the cells are disjoined. I think that in this action on cellulose and in the saccharification of the starch (wherewith compared the converting of proteids and fats is very subordinate) the chief signification of Monilia sitophila as technical mould should be sought.

Cane-sugar is hydrolised into invert-sugar, maltose into glucose; in both cases there is question of enzymes, as will be nearer explained below. The saccharification of the starch also, should be ascribed to the secretion of an enzyme (or perhaps two enzymes). This saccharification can best be observed when the mould is grown on boiled rice. The tough viscous matter is slowly liquefied; whilst at first the iodine reaction is distinctly blue, it gradually grows more reddish and finally all the starch proves to have vanished. The sugar formed is d-glucose, this follows from the extent of the rotation of the polarisation plane, compared with the reduction of FEHLING and from the formation of glucosazone with phenylhydrazine acetate. During the beginning of the hydrolysis however, the rotation proves to be much greater than corresponds with the cupric-oxide reduction, when this is rated as glucose; this is a consequence of the formation of dextrin as mid-product. If the dextrin is precipitated with alcohol then the rotation and the cupric-oxide-reducing power quite correspond with those of glucose. If the conversion products are daily determined, there is found in the beginning much dextrin and little glucose; by and by the latter increases whilst the former diminishes and at length disappears, when the glucose has reached a maximum (about 43 pCt. of the weight in rice); afterwards the glucose also

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decreases, evidently it is consumed by the mould. The auxanographic method of BEIJERINCK-WIJSMAN is difficult to apply whilst moulds as these soon completely overgrow an agar-agar- or gelatin-plate. Still the conversion of starch can be observed therewith, when an agar-plate is made and Monilia allowed to develop on it. When after a few days a dilute iodine solution is poured over the plate, it remains colourless at the place where the development of the mould has begun; round about a red zone is seen which gradually passes into the blue of the further portion of the plate.

From starch of different plants, under for the rest like circumstances, do not result equal quantities of sugar. I did not minutely investigate this fact; I only refer to it as it corresponds with what has before been described by me conjointly with Mr. PRINSEN GEERLIGS about Chlamydomucor Oryzae [1]).

The carbohydrates undergo still further conversions, as Monilia sitophila produces also alcohol and besides various esters; the latter cause the cultures to spread a pleasant odour, reminding of apple-essence. If these ethereal substances are distilled off they give a distinct jodoform reaction, whilst at a fractionated distillation of this product, the chief portion of the distillate, when shaken with benzoylchloride and caustic soda, produces a substance which by its smell is known as ethyl-benzoate.

Influence of the Nutrition on the Secretion of Enzymes.

The conversions of cane-sugar, maltose, and starch are caused by enzymes, which are secreted by the cells and so are to be found in the nutrient liquid. This can easily be shown by freeing the liquid with the help of filter-paper from the mycelium and the conidia of the mould and then mixing the filtrate with a solution of cane-sugar, maltose, or soluble starch, with addition of a little toluene or thymol, to prevent the growth of micro-organisms. After some time a conversion appears to have occurred, which can be measured by the change in the rotation of the polarisation plane or by the cupric-oxide reduction test, and can be qualitatively estimated by making the osazones. For control an experiment was made at the same time with the other half of the liquid, after it had been boiled a moment; with it the conversions did not take place. The enzyme (or better the mixture of enzymes) could be

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[1]) Verhandelingen Kon. Akad. v. Wet. 2e Sectie, Dl. IV, No. 2, 1895.

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precipitated with alcohol; after washing with alcohol a yellow-white powder was obtained, partly soluble in water. The solution proved to possess the properties of the original liquid, though in an attenuated degree; as is known for other cases, here also alcohol seems prejudicial to the activity of the enzymes. In pure state (albeit a mixture) they are surely not obtained in this way, because, as I hinted above, decomposition products of proteids occur in every culture liquid, and these are also partly precipitated by alcohol.

Are these enzymes secreted under all circumstances? It is known that for the glands of the intestinal canal of the higher animals, the experiments of PAVLOFF and his disciples have demonstrated, that the secretion of enzymes is indirectly influenced by the nutrition, but here the presence of the nervous system makes the phenomena extremely complex, so that the idea lay at hand to seek, whether not in plants something similar might be found in simpler form. For bacteria, FERMI [1]) had observed that a gelatin-liquefying enzyme is only produced in the presence of food containing proteids, whilst WORTMANN [2]) had thought to find a similar fact for diastase; but it should be called to mind, that the latter investigation was not done with pure cultures. BROWN and MORRIS [3]) have shown that embryos of grasses secrete no diastase when growing in strong sugar solutions. KATZ [4]) thinks that Penicillium glaucum would secrete no diastase when a sufficient quantity of cane-sugar or glucose is present in the nutrient liquid; to my opinion, however the method of investigation used does not allow to draw this conclusion. Finally DUCLAUX [5]) gives some brief remarks concerning Penicillium glaucum and a not nearer determined Aspergillus, which secrete certain enzymes only when they are fed in a special way.

Monilia sitophila enabled me more amply to study similar phenomena. As I said above, the proteolytic enzyme is secreted only with a particular nutrition, but I have not nearer investigated this point, because I wished to measure the quantity of enzyme and this can only be done exactly, when the conversion products can also be well determined. With the amylolytic enzyme we meet with the difficulty, that we do not know whether this is really a simple conversion or a co-operation of more enzymes. Hence, I wish only

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[1]) Centralblatt für Bakter. u. Parasitenk. Bd. X. 1891. p. 401.

[2]) Zeitschr. f. physiol. Chemie. Bd. VI. 1882. p. 287.

[3]) Journal of the Chem. Soc. LVII. 1890. p. 458.

[4]) Jahrb. f. wiss. Bot. 31. 1898. p. 599.

[5]) Traité de Microbiologie II, 1899, pg. 84—88.

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to observe, that a starch-saccharifying enzyme is secreted when starch and dextrin are given as carbon food, but furthermore also with maltose, glucose, glycerin, lactic acid, malic acid, and acetic acid, only the amount of enzyme is by no means always equally great. The sugar thereby resulting, was identified by the osazone in the case where the enzyme was produced in a glycerin-liquid; here, too, it was d-glucose. Presently it will be shown why this is of importance.

On the other hand, the inversion of cane-sugar or the hydrolysis of maltose can be very exactly determined. I therefore fixed my attention on these two conversions and in particular on the latter, because it was soon evident that invertase is secreted in all the examined cases, albeit not always in equally large quantities (i. e. when as carbon food were used cane-sugar, maltose, glucose, glycerin, lactic acid, malic acid, and acetic acid). Quite different is the case with the maltose-enzyme, which I will give the name of *maltoglucase*.

As is known, an enzyme forming glucose, has been named glukase by BEIJERINCK and the German investigators. If the view of CROFT HILL [1]) that this conversion is a reverse action proves to be right, this name already gives rise to confusion, still more, however, if one and the same plant, as Monilia sitophila, secretes two enzymes, both forming glucose, one from dextrin (starch), the other from maltose. The nomenclature of DUCLAUX and his school would be "maltase", but here we find the same difficulty, for starch is not always converted in the same way by different enzymes; would it then be correct to speak of amylase in every case? The confusion becomes still greater by the fact that maltase is quite another thing for DUCLAUX than for BEIJERINCK and WIJSMAN. In my opinion the problem is best solved by using a double name and thus to speak of maltoglucase. The same nomenclature can be used in all cases where the product of the conversion is well known and simple.

Maltoglucase now (with a single exception of which presently more), is exclusively secreted at the nutrition of Monilia sitophila with certain carbohydrates, and that in a very unequal degree. The following non-carbohydrates, when serving as carbon food, give no rise to the secretion of the here meant enzyme: glycerin, erythrite, mannite, dulcite, isodulcite, sorbite, ethyl-acetate, acetic acid, lactic acid, malic acid, succinic acid, citric acid, glycocol,

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[1]) Journal of the Chem. Soc. 1898, p. 634.

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asparagin and tyrosin. In this list we find, among others, glycerin; in this liquid, in which no maltoglucase is produced, the amylolytic enzyme is found, and it is worth mentioning that it causes the production of glucose from the starch. This proves that here DUCLAUX's [1]) view is untenable, according to which in all cases, where, by the action of enzymes glucose takes rise from starch, there would first be formed maltose, which then, by another enzyme would be converted into glucose. Nor is the opinion of BEIJERINCK [2]) tenable in this case; his glucase would convert as well maltose, as erythro- and malto-dextrin into glucose. Hence we must admit that here the conversion into glucose is effected, either by a single enzyme, or by two enzymes, one of which converts starch into dextrin and perhaps corresponds with one of the constituents of diastase (i. e. the dextrinase of WIJSMAN [3]), the other hydrolysing dextrin into glucose.

Neither does Monilia sitophila secrete malto-glucase at nutrition with the following carbohydrates: arabin, l-arabinose, lactose and inulin (when Ammonium salts or nitrates serve as source of nitrogen). Here it should be borne in mind that my meaning is of course: no measurable quantities of maltoglucase. As the most accurate measurements may be done by means of the polarimeter I have used this instrument and have then considered changes of rotation below 0.10° as to lie within the limit of errors. Only arabinose lay about near this limit, but if this might point to the secretion of traces of enzyme, it could still be attributed to impurities. That these can indeed be of influence, was for instance shown with lactose. Pure commercial milk-sugar gave rise to the secretion of small quantities of enzyme (when a 5 pCt. solution was used the decrease in rotation was 0.36° in 3 days), but after I had purified it and then repeated the experiment no enzyme was secreted anymore.

Large quantities of maltoglucase are secreted, when the mould can use, as source of carbon, first of all raffinose or maltose, further, commercial dextrin or starch. In less degree cellulose gives rise to the secretion of the enzyme; still less galactose, xylose, glycogen, whilst last of all, come cane-sugar and d-fructose. With the last mentioned carbohydrates, peptone stands about on a level, whilst also in milk a slight quantity of enzyme is secreted; in this latter

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[1]) Traité de Microbiologie. II. 1899, p. 471 vlg.

[2]) Centralbl. f. Bakter. u. Parasitenk. 2e Abth. I. 1895, p. 221.

[3]) De diastase beschouwd als mengsel van maltase en dextrinase. Amsterdam 1889.

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case the cause cannot be sought in the lactose or the fat, so that here, too, the proteids of the milk must cause the secretion of the maltoglucase. Would not the carbohydrate-rest, which probably occurs in the proteid molecule, explain this fact?

It is in general the best-feeding carbohydrates, which cause the secretion of the greatest quantity of enzyme, but this does not include that there should be a direct relation, as proved by the following data:

Carbon food.	Relative quantity of secreted enzyme.	Quantity of mould obtained (dry matter).
10 pCt. raffinose	10.17	257 mGrs.
5 » dextrin	7.17	61 »
2,5 » maltose	5.14	41 »
5 » galactose	0.68	12 »
5 » glycogen	0.55	36 »
5 » cane-sugar	0.26	21 »
5 » lactose	0	30 »
5 » peptone	0.50	124 »

Another question to be answered was, whether, at the nutrition with the same substance but in varying quantities, there exists a direct relation between the quantity of the food and that of the secreted maltoglucase.

For the measurement of the relative quantity of enzyme, there are two ways: one is to observe how much time is required to convert equal quantities of the substance; the quantities of enzyme are then inversely proportionate to those times. Or, the quantities of substance, converted in equal times, are determined; in the beginning of the reaction these quantities are proportionate to the quantities of the enzyme. I have used the latter method after first having convinced myself of its usefulness by some preliminary experiments.

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The result of a series of experiments, taken in particular with raffinose, but also with maltose, was that the quantity of secreted enzyme rises with the amount of sugar given as food; so long as the latter is still present in a slight quantity, both increase almost proportionately. But as the concentration of the solution becomes greater, the increase of the secreted enzyme is seen to diminish, until it reaches a maximum, then to decrease at still higher concentration of food. This maximum lies for raffinose and maltose at a concentration of about 10 pCt.

Very possibly the idea might arise that in these strong raffinose and maltose solutions, the quantity of secreted enzyme becomes smaller by the great osmotic pression of the solution; this is not however the cause. In order thereabout to get certainty, I have mixed the raffinose and maltose solutions with dilute glycerin of such a strength that all solutions of varying sugar amount were isotonic. Glycerin was taken, because, as said above, it has no influence on the secretion of maltoglucase, neither does it act accelerating or retarding on the reaction of the enzyme, at least not in the used concentrations (as shown by other particular experiments). It was thus proved that under these conditions the quantity of secreted enzyme mounted likewise with increasing concentration, about to the same maximum; only the proportionality at feeble concentrations was sometimes less striking than in absence of glycerin. This is probably a consequence of the more vigorous development of the mycelium of Monilia when, together with the slight amount of raffinose or maltose, glycerin was also present, which fact was already briefly discussed above.

The question arises whether the different amounts of secreted enzyme, cannot be a consequence of the degree of development of the mould. For it might be thought that each cell of the mycelium, so long as it lives, secretes a certain constant quantity of enzyme, hence, that the more vigorously the mycelium has developed, the more enzyme will be secreted. I have tried to answer this question by also weighing in every case the crop of mould obtained (after drying). I will give one of the series of figures thus obtained.

In column I is found the constitution of the nutrient liquid, in column II the crop of mycelium in mgrs., in column III the quantity of secreted enzyme, whilst column IV indicates the quantity of enzyme secreted on 100 mgrs. of dry matter of the mycelium.

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	I.					II.	III.	IV.
1.	0	pCt.	raffinose	3.27	pCt. glycerin	25	0	0
2.	0	»	»	3.27	» »	21	0	0
3.	0.16	»	»	3.24	» »	141	0.32	0.23
4.	0.31	»	»	3.22	» »	116	0.24	0.21
5.	0.62	»	»	3.16	» »	208	0.57	0.27
6.	1.25	»	»	3.06	» »	211	1.03	0.49
7.	2.5	«	«	2.86	» »	230	1.77	0.77
8.	5	»	»	2.46	» »	257	3.16	1.23
9.	10	»	»	1.63	» »	342	3.87	1.13
10.	20	»	»	0	» »	528	3.74	0.71

When considering only the figures of rows 3, 4 and 5 in column IV, they are rather alike, but further there hardly appears any relation between the development of the mycelium and the quantity of secreted enzyme. Though it will not be possible to make a pure comparison, as then for the total weight of mould obtained allowance should be made for the portion present in the air, the dead cells, etc., still rows 9 and 10 show that the mass of mycelium can increase considerably (and here in both cases all was nearly completely immersed) whilst the quantities of secreted enzyme have remained rather unchanged.

Whilst we saw already that the nature of the food is of great influence on the secreting or not secreting of maltoglucase, it is now evident that the quantity of the food offered, likewise exerts influence on the quantity of secreted enzyme, in such a sense, that both increase conjointly, but that very great quantities of food act prejudicially on the secretion of the enzyme.

There is a certain disposition to admit that the secretion of enzymes in general would be the consequence of the want of certain nutrients, and would indicate, as it were, a hungry condition of the cell. The investigations here communicated do not agree with this view; they contain a warning against too rashly drawing conclusions on this head.

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Chemistrie. — Professor H. W. BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS entitled: "*Determination of the decrease of vapour-tension of a solution of Na Cl at higher temperatures.*"

(Read January 26, 1901).

Introduction.

Continuing some earlier researches,[1]) I have performed some measurements between 50° and 80° with regard to the decrease of vapour tension of Na Cl solutions. The apparatus, which I used for that purpose was a small BREMER oil-tensimeter[2]). The source of heat was an oil-bath, the temperature of which could be kept constant within 0.15° by means of a stirring apparatus and an electrical regulator. The accuracy of the method applied did not appear to be greater than 1 m.m. of oil. This is the reason, why I could not continue the measurements below the concentration 0,1 gram molecule per 1000 grams of H_2O. The results were as follows:

Concentration in gram mols. of Na Cl per 1000 grams of H_2O	Temperature.	Observed difference in m.m. of oil at the observation temperature.	Difference in m.m. of H_2O at 4°.
0.7414	52°.15	36.5	32.5
	54°.0	40.0	35.6
	60°.38	55.0	48.7
	68°.75	80.0	70.5
	70°.9	88.0	77.4
0.4958	56°.4	30.0	26.6
	64°.6	43.5	38.4
	74°.0	65.0	57.0
	77°.0	75.0	65.6
0.0996	54°.4	5.5	4.9
	63°.0	7.0	6.2
	71°.0	10.0	8.8
	73°.0	11.0	9.7
	84°.8	21.0	18.2

[1]) Report Kon. Akad. v. Wet. 30 Sept. (1899) p. 160; 27 Jan. (1900) p. 471; 21 April (1900) p. 714.

[2]) Rec. des Trav. Chim. des Pays-Bas 6, 126.

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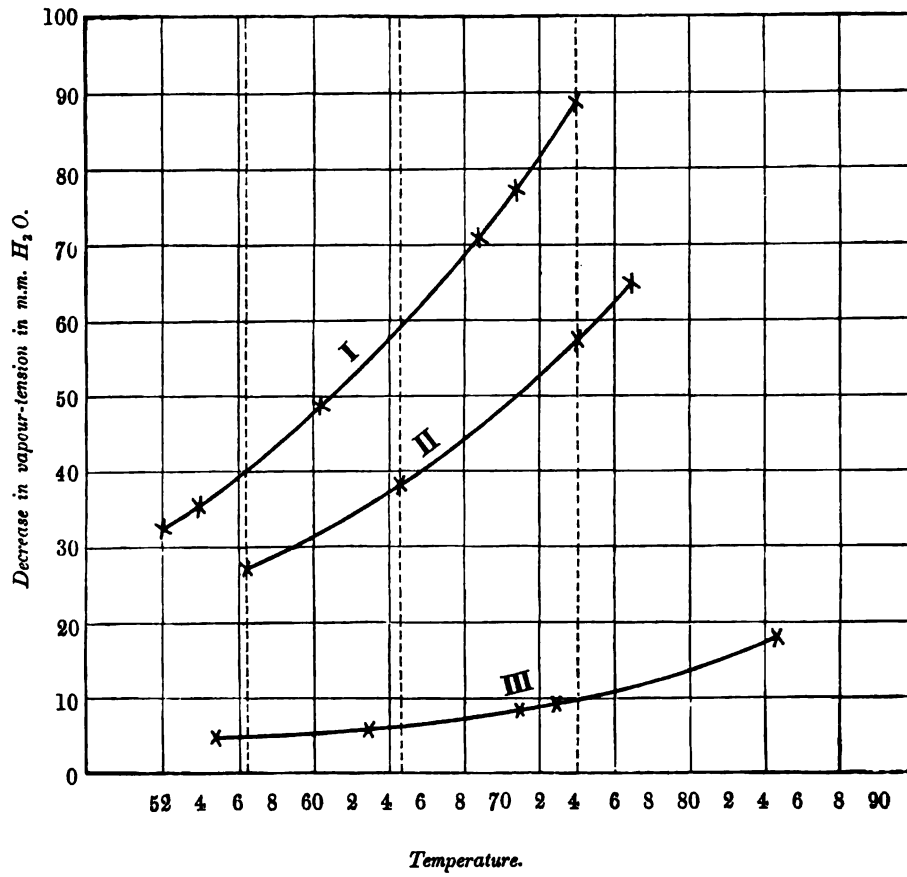
To express the observed difference of level of the oil at different temperatures in m.m. of H_2O at 4°, the specific gravity of the olive oil was determined at various temperatures.

By means of the figures occurring in the fourth column, the decrease in the vapour tension of the three different solutions is shown at different temperatures in the following graphical representation.



The molecular decreases of the vapour tensions of the three solutions have been calculated for three temperatures: 56,4°, 64,6° and 74,0°.

The pressures of II were known for these temperatures; for I and III they have been obtained by graphical interpolations. The value of I at 74° has been got by a small extrapolation which, on account of the regular course of the line, is sufficiently accurate.

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Concentration	Temperature	Decrease in vapour tension in m.m. H_2O at 4°.	Molecular decrease in vapour tension Hg. at 0°.	i
0.7414	74°	89.0	8.83	1.77
0.4958	»	57.0	8.49	1.7
0.0996	»	10.8	7.8	1.6
0.7414	64.6°	59.0	5.85	1.77
0.4958	»	38.4	5.66	1.7
0.0996	»	6.5	4.8	1.5
0.7414	56.4°	39.8	3.95	1.75
0.4958	»	26.6	3.92	1.7
0.0996	»	5	3.4	1.5

The value of i has been obtained by dividing the experimentally found decrease in vapour tension by the calculated decrease, when no electrolytic dissociation had taken place. This theoretical value was obtained by means of VAN 'T HOFF's equation

$$\Delta p = \frac{n}{N} p .$$

If we now take a solution, which contains 1 gram mol. per 1000 grams of water and then ask what will be the decrease of the vapour tension of this solution at 74°, then the data are $n = 1$, $N = 55{,}6$ and $p = 276{,}6$ (REGNAULT) and consequently

$$\Delta p_{74^\circ} = \frac{1}{55{,}6} \times 276{,}6 = 4{,}98.$$

For 64,6° we find

$$\Delta p^{64{,}6} = \frac{1}{55{,}6} \times 183{,}7 = 3{,}30$$

and for 56,4°

$$\Delta p_{56{,}4} = \frac{1}{55{,}6} \times 125{,}65 = 2{,}26.$$

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Review of the Results.

Although better results are obtainable by using my micromanometer and boiling apparatus, the above method is still accurate enough to demonstrate the course of the molecular decrease of vapour tension as a function of the concentration. It appears from the experiments, that the molecular decrease of vapour tension does not show a minimum between 56° and 74°, but continually increases with the concentration.

To pronounce on the strength of these results, that the minimum, which has been found at 100° by means of the boiling point method between the concentrations 0,5 and 0,1 gram mol. per 1000 grams of H_2O, has already disappeared at 74° appears to me to be too sweeping. A repetition of these measurements by means of a more accurate method might enable us to answer this interesting question, but provisionally there is not much chance for this. The great difficulty is caused by the temperature. In order to proceed further, it would be required to keep the bath constant at each temperature within 0,05°; this has been unattainable as yet. It is perhaps possible to obtain a bath of a very constant temperature by allowing some liquid or other to boil under a pressure, which is kept constant to 1 m.m. of H_2O by the manostat [1]) but in how far this method will be a practical one for my purpose remains to be seen.

The state of affairs at the moment is as follows:

1. It has been found by means of the micromanometer that at 0°, between the concentrations 0.05 and 2 gram mol. per 1000 grams of H_2O, the molecular decrease of vapour tension increases with the concentration in the case of either electrolytes or non-electrolytes except with KNO_3.

2. An increase of the molecular decrease of vapour tension, when the concentration is increased has also been observed with the oil-tensimeter from 56°—74° between the concentration 0.1 and 1 gram per 1000 grams of H_2O in the case of Na Cl solutions.

3. The same progressive change of the molecular increase of the boiling point has been observed with my boiling apparatus at 100° for solutions of Na Cl and K Cl between the concentrations $\pm$ 0.3 and 1.0 gram mol. that is to say an increase of the molecular increase of the boiling point with a rise of the concentration.

Between the concentrations 0.1 and 0.5 gram mol. at about 0.3

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[1]) Report Nov. 27 1897.

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mol., a minimum of the molecular increase of the boiling point was, however, observed with this method and with this a minimum of i, which did not appear in the sets of measurements 1 and 2. It is very remarkable, that it was also found by the boiling point method, that solutions of KNO_3 of the concentration 0.05 to 1 gram mol. make an exception to the general rule.

It is strange, that this phenomenon has not yet been brought to light by the freezing point method.

Amsterdam, Chem. Lab. Univers. January 1901.

Chemistry. — Professor H. W. BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS entitled: "*Some observations on the results obtained in the determination of the decrease in vapour tension and of the lowering of the freezing point of solutions, which are not very dilute.*"

(Read January 26, 1901).

With the aid of the theory of the thermodynamic potential, VAN LAAR [1]) has calculated accurate formulae for the decrease of the vapour tension, elevation of the boiling point and lowering of the freezing point. These formulae have the advantage, that they may be applied to dilute as well as to more concentrated solutions, which renders it possible to compare quantitatively the results of investigations of solutions, which are not very dilute.

The formula for the decrease of the vapour tension is as follows:

$$\log \frac{p_0}{p} = f - \log c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

p_0 = vapour tension of the solvent
p = " " " " solution
c = concentration = $\frac{n}{N+n}$
f is a quantity which = 0 for dilute solutions.

For the elevation of the boiling point we have the equation:

$$\Delta\tau = \tau - \tau^0 = \frac{R\tau\tau_0}{W}(f - \log c). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[1]) Zeitschr. Physik. Chemie 15, S. 457 (1894).

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τ and τ_0 are the absolute boiling points of solvent and solution.

W = molecular heat of evaporation of the solvent.

R = gas-constant.

For the lowering of the freezing point we have the analogous formula

$$\Delta\tau = \tau_0 - \tau = \frac{R\,\tau\,\tau_0}{S}(f - \log c) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which S means the molecular heat of fusion of the solvent.

As the values of f in the different formulae are only comparable at the same temperature, we can for instance calculate for the temperature 0° the relation, which must exist between the lowering of the freezing point and the lowering of the vapour tension.

From (1) and (3) follows:

$$\log\frac{p_0}{p} = \frac{\Delta\tau}{\tau\tau^0}\cdot\frac{S}{R}.$$

or

$$\log\frac{p_0}{p} = \Delta\tau\,\frac{S}{R\,\tau_0^2}\cdot\frac{\tau_0}{\tau} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In the case that water is chosen as a solvent we have:

$$\frac{S}{R\,\tau_0^2} = \frac{1}{1.863} \times \frac{18.016}{1000}$$

$$\frac{\tau_0}{\tau} = \frac{\tau_0}{\tau_0 - \Delta\tau} = \frac{1}{1 - \frac{\Delta\tau}{\tau_0}} = 1 + \frac{\Delta\tau}{\tau^0} + \quad . \quad . \quad . \quad . \quad .$$

The equation (4) therefore becomes:

$$\log\frac{p_0}{p} = \frac{\Delta\tau}{1.863} \times \frac{18.016}{1000}\left(1 + \frac{\tau^0}{\Delta\tau} + \quad . \quad . \quad .\right) \quad . \quad . \quad . \quad . \quad (5)$$

If, however, we neglect the powers higher than 2 then

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$$log \frac{p_0}{p} = log \frac{p_0}{p_0 - \Delta p} = log \frac{1}{1 - \frac{\Delta p}{p_0}} =$$

$$= - log \left(1 - \frac{\Delta p}{p_0}\right) = \frac{\Delta p}{p_0} + \tfrac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2.$$

Consequently

$$\frac{\Delta p}{p_0} + \tfrac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2 = \frac{\Delta \tau}{1.863}\left(1 + \frac{\Delta \tau}{\tau_0}\right) \times \frac{18.016}{1000} \quad . \quad . \quad . \quad . \quad (6)$$

If we now calculate $\frac{\Delta p}{p^0}$ from RAOULT's [1]) determinations of the freezing point by means of equation (6), we obtain the following figures for cane-sugar.

Cane-sugar.

TABLE I.

Concentration in gr. mol. per 1000 gr. H_2O	$\Delta\tau$	$\frac{\Delta\tau}{1,863}$	$\frac{\Delta\tau}{1,863}\left(1 + \frac{\Delta\tau}{\tau_0}\right)$	$\frac{\Delta p}{p_0} + \frac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2$	$\frac{\Delta p}{p_0}$
1.0107	2.0897	1.122	1.130	0.02036	0.02015
0.5056	0.9892	0.5310	0.5329	0.009600	0.009554
0.2500	0.4806	0.2580	0.2585	0.004657	0.004646
0.1250	0.2372	0.1273	0.1274	0.002295	0.002292
0.0652	0.1230	0.06602	0.06605	0.001190	0.001189
0.0285	0.0532	0.02856	0.02857	0.0005147	0.005147

By multiplying the figures in the last column by $p_0 = 4,62$, we obtain the decrease of the vapour tension corresponding to the lowering of the freezing point observed by RAOULT.

In order to be able to compare these figures with my latest results,

[1]) Zeitschr. f. Physik. Chemie 27, S. 638 (1898).

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obtained with solutions of cane-sugar [1]), I have calculated by interpolation the decreases of the vapour tensions for the same concentrations as used by RAOULT in his determinations. The result is as follows:

TABLE II.

Concentration	Δp in m.m. of Hg RAOULT.	Δp in m.m. of Hg SMITS.	Difference	%
1.0107	0.09289	0.09090	— 0.00199	— 2.1
0.5056	0.04414	0.04446	+ 0.00032	+ 0.7
0.2500	0.02146	0.02167	+ 0.00021	+ 0.9
0.1250	0.01059	0.01072	+ 0.00013	+ 1.0
0.0652	0.00549	0.00557	+ 0.00008	+ 1.5
0.0285	0.00238	0.00240	+ 0.00002	+ 0.8

The agreement is, therefore, a very satisfactory one, the differences being within the range of the experimental errors.

If we now calculate in a similar manner the decrease of the vapour tension from the lowering of the freezing point of Na Cl-solutions observed by RAOULT and then compare these figures with those obtained by direct measurement, we find the following:

Sodium chloride.

TABLE III.

Concentration	$\Delta\tau$	$\frac{1.863}{\Delta\tau}$	$\frac{\Delta\tau}{1.863}\left(1+\frac{\Delta\tau}{\tau^0}\right)$	$\frac{\Delta p}{p_0}+\frac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2$	$\frac{\Delta p}{p_0}$
1.0000	3.4237	1.838	1.8610	0.03353	0.03297
0.4887	1.6754	0.8993	0.9048	0.01630	0.01617
0.2393	0.8211	0.4407	0.4420	0.007962	0.007930
0.1179	0.4077	0.2188	0.2191	0.003947	0.003939
0.05829	0.2073	0.1113	0.1114	0.002007	0.002005

[1]) Report Kon. Akad. v. Wet. 30 Sept. 1899, p. 162. It is stated there that the greatest concentration is 1.0811; this should be 1.0089.

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TABLE IV.

Concentration	Δp in m.m. of Hg RAOULT.	Δp in m.m. of Hg SMITS.	Difference	%
1.0000	0.1523	0.1437	0.00860	— 5.6
0.4887	0.07470	0.06937	0.00533	— 7
0.2393	0.03664	0.03367	0.00297	— 8
0.1179	0.01820	0.01646	0.00174	— 9.5
0.0582	0.00926	0.00800	0.00126	—13.6

Here there is absolutely no question of agreement and at the same time we observe, that the difference continually increases with the dilution.

Before proceeding further I will just show, that if I had compared RAOULT's results with mine by calculating the factor i, I really would have committed an error, although as we will see presently, this error is so small that it is only revealed at the greatest concentration.

According to VAN 'T HOFF, the factor i may be calculated from the decrease of the vapour tension and the lowering of the freezing point by means of the formulae:

$$i_d = \frac{\Delta p}{p_0} \cdot \frac{N}{n} \quad \ldots\ldots\ldots \quad (7)$$

and

$$i_v = \Delta\tau \frac{S}{R\tau_0^2} \cdot \frac{N}{n} \quad \ldots\ldots\ldots \quad (8)$$

From this follows:

$$\frac{\Delta p}{p_0} = \Delta\tau \frac{S}{R\tau_0^2} \quad \ldots\ldots\ldots \quad (9)$$

This equation is perfectly true for exceedingly diluted solutions, but it no longer applies to solutions, which are not very much diluted. For these, VAN LAAR has found indeed the relation (4) instead of the equation (9):

$$log \frac{p_0}{p} = \Delta\tau \frac{S}{R\tau_0^2} \cdot \frac{\tau_0}{\tau}$$

or

$$\frac{\Delta p}{p_0} + \frac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2 = \Delta\tau \frac{S}{R\tau_0^2} \cdot \frac{\tau_0}{\tau}$$

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From this we see that for solutions, which are not very much diluted both sides of the equation (9) are too small. If the error were the same in both sides it would naturally be eliminated from the difference of the equations (7) and (8), so that a comparison of the results of solutions, which are not very much diluted, might be arrived at by applying the equations (7) and (8).

If the equations (7) and (8) were of universal application, then we ought to find for all concentrations

$$i_d = i_v$$

and because

$$i_d + \tfrac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2 \frac{N}{n} = i_v \frac{\tau_0}{\tau}$$

we should find

$$\tfrac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2 \frac{N}{n} = i_v \left(\frac{\tau_0}{\tau} - 1\right) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This equation is no longer true for solutions which are not very much diluted, for in that case we find

$$\tfrac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2 \frac{N}{n} > i_v \left(\frac{\tau_0}{\tau} - 1\right) . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

For most of the solutions which have been examined this difference is, however, so small, that it may be neglected, but when the greatest concentration 1 gram mol. per 1000 grams of water is reached it becomes distinctly perceptible. This is easily shown by the following table in which i has been calculated from the molecular lowering of the freezing point, and from the molecular decrease of the vapour tension by dividing these by 1.863, and 0.08316 respectively.

Cane-sugar.

TABLE V.

Concentration.	mol. lowering of the freezing point.	mol. decrease of the vapour tension.	i RAOULT	i SMITS	Difference in %
1.0107	2.0676	0.08994	1.110	1.082	−2.5
0.5056	1.9565	0.08761	1.050	1.057	+0.7
0.2500	1.9224	0.08668	1.033	1.042	+0.9
0.1250	1.8976	0.08576	1.020	1.031	+1
0.0652	1.8860	0.08543	1.013	1.027	+1.4
0.0284	1.8667	0.08421	1.004	1.013	+0.9

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Sodium chloride.

TABLE VI.

Concentration.	mol. lowering of the freezing point.	mol. decrease of the vapour tension.	i RAOULT	i SMITS	Difference in %
1.0000	3.4237	0.1437	1.838	1.728	— 6.1
0.4887	3.4283	0.1419	1.840	1.707	— 7
0.2393	3.4313	0.1407	1.842	1.692	— 8
0.1179	3.4581	0.1396	1.856	1.679	— 9.5
0.05829	3.5564	0.1372	1.909	1.650	—13.6

If we now compare the differences in the last column of these tables with those of the fifth column of tables II and IV, we see that on the whole they agree with each other; only at the greatest concentration the differences are 0.4 and 0.5 percent greater. For this concentration the disparity, as represented by equation (11), is very perceptible.

If, for instance, we calculate for the concentration 1.0107 gram mols. (Table V)

$$\frac{1}{2}\left(\frac{\Delta p}{p_0}\right)^2 \frac{N}{n} \text{ and } i_v\left(\frac{\tau_0}{\tau} - 1\right)$$

we find for the first quantity the value 0,013 and for the second 0,008. If we now add to RAOULT's i 0,008 and to my own 0,012, we naturally obtain again, just as in table II, a difference of 2,1 percent for this concentration. In the same manner the difference of 0,5 percent disappears at the greatest concentration of Na Cl.

The foregoing teaches us up to what concentration we can in this case make a comparison by means of i. We are therefore, obliged to stop at the concentration 1 gram molecule. Up to the concentration 1 gram mol. the values of i must agree within 0,1—0,2 percent by whatever method they have been obtained. In this we must, however, not forget that the factor i is not to be considered as a dissociation factor, but as a quantity of which we do not as yet know the true significance.

I consider it an indisputable fact that i generally increases with the concentration in solutions which are *not very dilute.*

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The determinations of the vapour tensions at 0° and between 50° and 70° [1]) and also the determinations of the boiling point (from the concentration ± 0,3 gram mol. up to higher concentrations) lead to this conclusion.

The fact that RAOULT, who continued his experiments up to the concentration 1 gram. mol., observed a fall of i with an increase of the concentration points to an error. RAOULT ought also to have observed a rise of i with the concentration of his *stronger solutions*.

The possibility of an error in RAOULT's determinations is also corroberated by the latest communication from CHROUSTCHOFF [2]) entitled „Recherches Cryoscopiques" where the thermometer has been replaced by a thermo-element accurate to 0.0005°. In the case of Na Cl, he found between the concentrations $^1/_4$ and $^1/_{64}$ gram mol. a constant molecular lowering of the freezing point. In the case of K Br, he found between the concentrations $^1/_4$ and $^1/_{128}$ gram mol. *an increase of the molecular lowering of the freezing point with increasing concentration.* In the case of $K_2 SO_4$ however, he noticed the reverse change between the concentrations $^1/_4$ and $^1/_{64}$ gram molecule. The fact that a small alteration in the method influences the results and even alters the course proves that the freezing point method is attended by unknown sources of error, in the case of electrolytes at any rate. I consider that CHROUSTCHOFF has made a great improvement by determining the concentration of the solution after the separation of ice.

Finally there are also determinations of the freezing point where a minimum of i has been found; I obtained this also by means of the method of boiling in the case of solutions of Na Cl or K Cl. JONES, CHAMBERS and FRAZER [3]) found minima for the solutions of the chlorides and bromides of Mg, Ca, Ba and further for $Cu SO_4$, $H_3 PO_4$, H Cl, $C H_3 CO O Na$, $Cd I_2$, $Sr I_2$ and $Zn Cl_2$; as a rule these minima lie below the concentration 0.5 mol.

Finally I wish to express my hearty thanks to Mr. VAN LAAR for the assistance he has rendered.

Amsterdam, Chem. Lab. Univers. Jan. 1901.

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1) See preceding article.

2) Comptes Rendus CXXXI p. 883 (1900).

3) Amer. Chem. Journal Vol. 23, p. 89 and 512 (1900).

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Physics. — „*The equation of state and the theory of cyclic motion.*" By Prof. J. D. VAN DER WAALS.

It may be taken for granted that in the deduction of the equation of state the molecules at all temperatures under all pressures are assumed to be invariable systems. As soon, therefore, as association to more complex systems takes place, at which even the number of atom systems (molecules) changes, this equation of state does not hold good. But even when the systems are subjected to a less radical change and e. g. the dimensions of the molecules in different circumstances change, a and b can no longer be thought constant. It is noteworthy that for the very first substance at which I tested my equation of state (CO_2 according to the experiments of ANDREWS) a value of b was found increasing with the temperature, and that the only reason why I have not taken into account the variability, was that the dependence of b on the temperature is unknown.

The very fact that the value of the specific heat at constant volume for complex molecules does not at all square with that found for monatomic molecules, shows that besides molecular motion we shall also have to accept internal motion (atomic motion). The fact that this atomic motion is more violent at higher values of T justifies the thought, that the molecules are really larger at higher temperatures than at lower ones. The equation of state with constant value of a and b can therefore not hold good for substances with any but monatomic molecules. That it has been applied to substances with very complex molecules can be justified as an approximation only when we assume that the internal forces which bind the atoms together, are so considerable that by approximation the expansion of the molecules may be neglected. Just as a liquid at a low temperature, so if it is subjected to a great internal pressure, expands but little, we may expect the expansion of a molecule to be slight, as the molecule may be considered as an atomic system with a perhaps much higher internal pressure.

That we shall have to consider the molecules themselves as variable with p and T and that there is therefore question of an equation of state of the molecule itself, I have already indicated in a communication, inserted in the Proceedings of the meeting of Oct. 29th 1898, p. 138, in the following words: "The equation (f) may be considered to contain the conditions for the stationary state of the molecules." And in the way indicated there, so by means of the virial-equation, I had since deduced an equation of state for the molecule; but as many questions which arise in the

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course of the deduction, could not be decided with perfect certainty, and as it was impossible to fix on any grounds except those of probability the relation which exists between the vis viva of the atomic motion and that of the molecular motion at different temperatures, and in how far that relation can be variable at different degrees of density of the substance, I have cast about for other means to see in how far the form I am going to give would hold good at least as an approximation. First of all by a way which may be called chiefly thermodynamic, secondly by availing ourselves of the theory of the cyclic motion.

From the equation of the virial we find l. c. also for substances with complex molecules, the equation of state:

$$(p + N)(v - b) = \Sigma \frac{1}{3} m V_z^2,$$

whereas according to the method of deduction followed there, it is not necessary to assume the molecules to be spherical. It only appears that the value of b, being a multiple of the volume of the molecules which themselves are in motion, must be thought variable.

For the value of $\frac{\partial \varepsilon}{\partial v_T}$, which may be determined by means of $T\left(\frac{dp}{dt}\right)_v - p$, we find from:

$$p = \frac{RT}{v-b} - N$$

$$\frac{\partial \varepsilon}{\partial v_T} = N - T\left(\frac{\partial N}{\partial T}\right)_v + \frac{RT^2}{(v-b)^2}\left(\frac{db}{dT}\right)_v.$$

Even if we assume N as function of v to be known, this equation is not to be integrated, if we do not know in what way b is dependent on v. But probably ε will have the following shape:

$$\varepsilon = F(T) + P_v - T\left(\frac{dP_v}{dT}\right)_v + P_b - T\left(\frac{dP_b}{dT}\right).$$

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If we namely imagine a substance with invariable molecules and a molecular pressure not dependent on T, we find:

$$\varepsilon = F(T) + P_v,$$

in which P_v is such a function of v, that $N = \frac{dP_v}{dv}$.

If the molecular pressure should be a function of the temperature, we find, as according to thermodynamic rules is always the case when the force depends on T, also the term $-T\left(\frac{dP_v}{dT}\right)_v$, and therefore:

$$\varepsilon = F(T) + P_v - T\left(\frac{dP_v}{dT}\right)_v.$$

If the molecules should also be variable, and the atoms which attract each other at varying distances from each other, the whole energy will also vary with that which the atoms in the molecular-aggregate have with regard to each other. Take P_b as such a function of b and T, that $\left(\frac{dP}{db}\right)_T$, as will presently appear, is in close relation with the forces which keep the molecule together, then two new terms will be added to the value of ε, at least if we think also these forces as variable with T, and we shall find the form of ε given above.

If we deduce from this $\left(\frac{d\varepsilon}{dv}\right)_T$, we find:

$$N - T\left(\frac{dN}{dT}\right)_v + \frac{RT^2}{(v-b)^2}\left(\frac{db}{dT}\right)_T = \left(\frac{dP_v}{dv}\right)_T - T\frac{d^2P_v}{dT\,dv} + \left(\frac{dP_b}{db_T} - T\frac{d^2P_b}{dT\,db}\right)\left(\frac{db}{dv}\right)_T.$$

Having chosen the quantity P_v in such a way, that $N = \left(\frac{dP_v}{dv}\right)_T$ and therefore also $T\left(\frac{dN}{dT}\right)_v = T\frac{d^2P_v}{dT\,dv}$, the above equation is simplified to:

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$$\frac{RT^2}{(v-b)^2}\left(\frac{db}{dT}\right)_v = \left\{\left(\frac{dP_b}{db}\right)_T - T\frac{d^2P_b}{dT\,db}\right\}\left(\frac{db}{dv}\right)_T \quad . \quad . \quad . \quad (1)$$

This equation gives the relation between the partial differential quotients of b with respect to v and T, and it can be satisfied if we put $b-b_0 = f\left\{\frac{1}{v-b} + \frac{C}{RT}\right\}$, if namely the quantity C represents $\left(\frac{dP}{db}\right)_T$.

From $b-b_0 = f\left\{\frac{1}{v-b} + \frac{C}{RT}\right\}$ we deduce:

$$\left(\frac{db}{dT}\right)_v\left\{1-f'\left[\frac{1}{(v-b)^2} + \frac{\left(\frac{dC}{db}\right)_T}{RT}\right]\right\} = f'\left\{\frac{\left(\frac{dC}{dT}\right)_b}{RT} - \frac{C}{RT^2}\right\}$$

and

$$\left(\frac{db}{dv}\right)_T\left\{1-f'\left[\frac{1}{(v-b)^2} + \frac{\left(\frac{dC}{db}\right)_T}{RT}\right]\right\} = f'\left\{-\frac{1}{(v-b)^2}\right\}$$

or

$$\left(\frac{db}{dT}\right)_v \frac{1}{(v-b)^2} = \left(\frac{db}{dv}\right)_T\left\{\frac{C}{RT^2} - \frac{\left(\frac{dC}{dT}\right)_b}{RT}\right\}$$

or

$$\frac{RT^2}{(v-b)^2}\left(\frac{db}{dT}\right)_v = \left\{C - T\left(\frac{dC}{dT}\right)_b\right\}\left(\frac{db}{dv}\right)_T.$$

If $C = \left(\frac{dP_b}{db}\right)_T$, equation (1) is satisfied.

So the following formula may be a solution of (1):

$$b-b_0 = \frac{\gamma RT}{\frac{RT}{v-b} + C},$$

or

$$b-b_0 = \frac{\gamma RT}{p+N+C} = \frac{\gamma RT}{p + \left(\frac{dP_v}{dv}\right)_T + \left(\frac{dP_b}{db}\right)_T} \quad . \quad . \quad (2)$$

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Equation (2) is drawn up from the virial-equation by supposing that at a given temperature the relation between the vis viva of the atomic motion and that of the molecular motion is independent of the degree of density of the substance and may be represented for all temperatures by the constant value γ. The quantity b_0 in equation (2) represents the value of b, if $T = 0$ or at infinite pressure, and may be called the limiting volume of the molecule. It will therefore be in close relation with the volume of the atoms, of which the molecule is composed.

I did not, however, consider the way in which I had deduced (2) from the virial-equation, to be perfectly reliable, and specially the constancy of γ seemed open to doubt. It is true that the result of the thermodynamic deduction shows, that the given form (2) is a probable one, but it remains an open question whether other forms than the one given can also satisfy the partial differential equation (1) — leaving the question whether the chosen form of ε is the most general, out of account.

These considerations made me attempt to investigate what might be derived from the theory of cyclic motion for settling these questions.

Let us consider a gas at a given temperature and in a given volume as a system which is in cyclic motion [1]).

If we take as first case the gas consisting of material points but always, also in the following cases, as a statistic gas, so that all velocities occur equally at any time in any point in all directions.

Let the slowly variable coordinate be the volume; for the fluction of the rapidly variable coordinate we choose the number of shocks, to which an arbitrarily placed surface-unity, which we think impenetrable to substance, is subjected in one sec. If we call that number $\dot{s}$, the velocity of the material points may be proportionate to $\dot{s}$ and to a linear dimension of the volume, and the total vis viva may therefore be represented by:

$$L = Av^{2/3}\dot{s}^2.$$

We conclude also to this form, if we think, as CLAUSIUS already did, that the particles describe closed orbits, the linear dimensions of which, with change of volume, are proportionate to $\sqrt[3]{v}$, and if

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[1]) For the theory of the cyclic motion see: H. VON HELMHOLTZ, KRONECKER's Journal, Vol. 97, Pages 111 and 317. — L. BOLTZMANN, Vol. 98, pag. 68.

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we think for the fluction of the rapidly variable coordinate a quantity inversely proportionate to the time of revolution. The conception that $\dot{s}$ represents the number of shocks against a certain surface, has a closer analogy to the way in which MAXWELL applies the cyclic motion to the behaviour of two currents. In this case s would represent the number of particles which has touched the surface counted from an initial moment or if we prefer, which has passed the surface.

If from the given form of L, we derive the force which keeps the stationary system in the given volume, we find:

$$p = \frac{dL}{dv} = \frac{2}{3} A v^{-1/3} \dot{s}^2$$

or

$$pv = {}^2/_3 L,$$

the wellknown relation, which is generally given in the form:

$$pv = \Sigma \frac{1}{3} mn V^2$$

If we take secondly the case that the particles have a dimension which may not be neglected and at the same time that besides the pressure there are internal forces, the dimensions of the similar orbits have the ratio $(v-b)^{1/3}$ and we have therefore the relation:

$$L = A (v-b)^{2/3} \dot{s}^2$$

and we find:

$$p + \left(\frac{dP_b}{dv}\right) = \frac{dL}{dv} = {}^2/_3 A (v-b)^{-1/3} \dot{s}^2$$

or

$$\left\{p + \left(\frac{dP_v}{dv}\right)\right\} (v - b) = \frac{2}{3} L.$$

The case, that P_v is also a function of the temperature, can properly speaking not be treated according to the theory of cyclic motion, at least not in so far as it has been developed as yet, but it could not lead to a different result.

For $\frac{dL}{db}$ we find $- \left(p + \frac{dP_v}{dv}\right)$, which means that the molecules

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have to exercise as great a force in the opposite direction as is exercised on them by the stationary system.

If we now put the case that the molecules themselves form complex systems, the first question which arises is, whether the motion of the atoms satisfies the condition which must be put to a cyclic system. If we think that each of the atoms describes a closed orbit round the centre of gravity, then we may consider the number of times that the atom passes a certain point of its orbit again as fluction of a cyclic coordinate, and the distance from the point chosen to the centre of gravity as the slowly variable coordinate. Then the velocity might be put proportionate to the product of r and $\dot{s}$; but the question remains unsettled whether the forces which keep the atoms together work in such a way, that the orbits with another value of r and another of $\dot{s}$ may be considered as being similar. This difficulty has no weight for circular orbits. Nevertheless, it seems advisable to me not to consider in the first place circular orbits, but rather radial ones. In order to be able to apply the theory of the cyclic motion, we shall have to assume that the atoms move along their way with a constant velocity, and that at the end of their amplitude their motion is reversed by the collisions with other systems and by the force which compels them to form a system. If we take the distance counted from the centre of gravity and if r_0 is the shortest distance to which they can approach the centre of gravity, the velocity may be represented as proportionate to $(r-r_0)\dot{s}$, if $\dot{s}$ e. g. represents the number of times that the atom reaches the end of its course in 1 sec.

The vis viva of this motion is then $B(r-r_0)^2\dot{s}^2$.

For the case of diatomic molecules, we may therefore put:

$$L = A(v-b)^{2/3}\dot{s}^2 + B_1(r_1-r_{01})^2\dot{s}_1^2 + B_2(r_2-r_{02})^2\dot{s}_2^2.$$

Just as for simple molecules we find:

$$\frac{dL}{dv} = p + \frac{dP_v}{dv} = \frac{2}{3}A(v-b)^{-\frac{1}{3}}\dot{s}^2$$

or

$$\left(p + \frac{dP_v}{dv}\right)(v-b) = \frac{2}{3}A(v-b)^{\frac{2}{3}}\dot{s}^2 = \frac{2}{3}L_0.$$

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Before deriving the equation for the stationary state of the molecule, we must first settle the question, what the quantity b is according to this conception, and in what relation it is with $(r_1 - r_{01})$ and $(r_2 - r_{02})$. A spherical form for the complex molecule is now quite out of the question, even though the atoms should be spherical. The form is more like a cylinder, which has the direction of motion as axis, and one half of which has a section equal to the middle section of the first atom and the other half a section equal to that of the second atom. The molecule gets its smallest length when the atoms touch, and the distance of their centres is equal to $r_{01} + r_{02}$; its greatest length when the atoms are forced to reverse their motions. The molecule has therefore a variable length and so also a variable volume. But there is question of a mean value of the volume and in the same way we may choose mean values for r and r_0, so that, if the sections are S_1 and S_2, the equation is:

$$S_1 r_{01} + S_2 r_{02} = b_0$$

and

$$S_1 r_1 + S_2 r_2 = b.$$

If we now determine $\frac{dL}{db}$, and call the force which keeps the atoms together $\frac{dP_b}{db}$, we find:

$$\frac{dL}{db} = \frac{dP_b}{db} = -\frac{2}{3} A (v-b)^{-\frac{1}{3}} \dot{s}^2 + 2 B_1 (r_1 - r_{01}) \dot{s}_1^2 \frac{dr_1}{db} +$$

$$+ 2 B_2 (r_2 - r_{02}) \dot{s}_2^2 \frac{dr_2}{db}$$

or

$$\frac{dP_b}{db} + \left(p + \frac{dP_v}{dv}\right) = 2 \left\{ \frac{L_1}{r_1 - r_{01}} \frac{dr_1}{db} + \frac{L_2}{r_2 - r_{02}} \frac{dr_2}{db} \right\} \quad . \quad . \quad . \quad (3)$$

As we take the motions with a fixed centre of gravity as atomic motion, the following equations are of force:

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$$m_1 r_{01} = m_2 r_{02}$$

$$m_1 r_1 = m_2 r_2$$

$$m_1 (r_1 - r_{01}) = m_2 (r_2 - r_{02})$$

$$\frac{dr_1}{r_1 - r_{01}} = \frac{dr_2}{r_2 - r_{02}}$$

$$\frac{S_1 dr_1}{S_1 (r_1 - r_{01})} = \frac{S_2 dr_2}{S_2 (r_2 - r_{02})} = \frac{S_1 dr_1 + S_2 dr_2}{S_1 (r_1 - r_{01}) + S_2 (r_2 - r_{02})} = \frac{db}{b - b_0}.$$

So equation (3) furnishes

$$\left(p + \frac{dP_v}{dv} + \frac{dP_b}{db}\right)(b - b_0) = 2 (L_1 + L_2) \quad . \quad . \quad . \quad . \quad (4)$$

which equation assumes the form of (2), if we may put γRT for $2 (L_1 + L_2)$.

So we have still to deal with the same question, which we put above. But it was to be expected that the theory of cyclic motions would enable us to decide this question, as in many cases in these cyclic motions the vis viva had proved to be an integrating divisor of what we have to consider as heat which is to be supplied.

As the required heat will have to serve 1st to increase the vis viva of the molecular motion, and 2nd to perform the work of the different forces both internal and external we may put:

$$dQ = dL + \frac{dL}{dv} dv + db \left\{\frac{dL}{db} + \frac{dL}{dr_1}\frac{dr_1}{db} + \frac{dL}{dr_2}\frac{dr_2}{db}\right\}$$

or

$$dQ = dL + \frac{2}{3} A (v - b)^{-\frac{1}{3}} \dot{s}^2 dv - \frac{2}{3} A (v - b)^{-\frac{1}{3}} \dot{s}^2 db +$$

$$+ 2 B_1 (r_1 - r_{01}) \dot{s}_1^2 dr_1 + 2 B_2 (r_2 - r_{02}) \dot{s}_2^2 dr_2.$$

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Let us write:

$$L = L_0 + L_1 + L_2$$

$$dL_0 = \frac{2}{3} A (v-b)^{-\frac{1}{3}} \dot{s}^2 d(v-b) + A (v-b)^{\frac{2}{3}} d\dot{s}^2$$

$$dL_1 = 2 B_1 (r_1 - r_{01}) \dot{s}_1^2 dr_1 + B_1 (r_1 - r_{01})^2 d\dot{s}_1^2$$

$$dL_2 = 2 B_2 (r_2 - r_{02}) \dot{s}_2^2 dr_2 + B_2 (r_2 - r_{02})^2 d\dot{s}_2^2.$$

Now we may bring dQ under the following form:

$$dQ = L_0 \, d\,log\,[(v-b)^{2/3} L_0] + L_1 \, d\,log\,[(r_1-r_{01})^2 L_1] + L_2 \, d\,log\,[(r_2-r_{02})^2 L_2].$$

This form may be simplified if we take into consideration that $m_1 (r_1-r_{01}) = m_2 (r_2-r_{02})$ and $m_1 L_1 = m_2 L_2$, and that we may substitute $\frac{db}{b-b_0}$ for $\frac{dr_1}{r_1-r_{01}}$ and $\frac{dr_2}{r_2-r_{02}}$. We get then:

$$dQ = L_0 \, d\,log\,[(v-b)^{2/3} L_0] + (L_1 + L_2) \, d\,log\,[(b-b_0)^2 (L_1 + L_2)].$$

If we call L_0 the vis viva of the molecular motion L_m, then $L_1 + L_2$ is the vis viva of the atomic motion L_a; and we may also write:

$$dQ = L_m \, d\,log\,[(v-b)^{2/3} L_m] + L_a \, d\,log\,[(b-b_0)^2 L_a].$$

It is assumed as being beyond doubt that L_m is proportionate to the absolute temperature, and that therefore $\frac{dQ}{L_m}$ is a total differential.

Now

$$\frac{dQ}{L_m} = d\,log\,[(v-b)^{2/3} L_m] + \frac{L_a}{L_m} \, d\,log\,[(b-b_0)^2 L_a].$$

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The condition that the second member is a total differential is satisfied if we put $\frac{L_a}{L_m} = \text{constant} = \beta$ [1]).

As $L_m = \frac{3}{2} RT$, the entropy becomes:

$$\eta = R \left\{ log\,(v-b)\, T^{3/2} + log\,(b-b_0)^{3\beta}\, T^{\frac{3}{2}\beta} \right\}.$$

For the specific heat at constant volume we find from:

$$\left(\frac{d\eta}{dT}\right)_v = \frac{C_v}{T}$$

$$C_v = RT \left\{ \frac{3}{2}\left(\frac{1+\beta}{T}\right) + \frac{1 - \left(\frac{db}{dT}\right)_v}{v-b} + 3\beta \frac{\left(\frac{db}{dT}\right)_v}{b-b_0} \right\}$$

and for

$$C_{v=\infty} = \frac{3}{2} R(1+\beta) + 3\beta R \frac{T\left(\frac{db}{dT}\right)_{v=\infty}}{(b-b_0)}.$$

It is noteworthy, that we found for the molecular motion:

$$\left(p + \frac{dP_v}{dv}\right)(v-b) = {}^2/_3\, L_m,$$

whereas we find for the atomic motion:

$$\left\{p + \frac{dP_v}{dv} + \frac{dP_b}{db}\right\}(b-b_0) = 2\, L_a.$$

---

1) The condition that the second member is to be a total differential, would also be satisfied, if we could put $\frac{L_a}{L_m} = \varphi\,[L_a (b-b_0)^2]$. In so far, however, as I have been able to examine, no acceptable results are to be deduced from such a supposition. The supposition that $\frac{L_a}{L_m}$ is constant at all temperatures and under any pressure, is however still open to doubt, as long as the impossibility of such a supposition has not been proved.

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That the factor of the vis viva in the case of the atomic motion is three times as great as in the case of the molecular motion, is a consequence of the fact, that the molecular motion takes place in all directions, whereas the atomic motion is thought as in only one direction, and at any rate shows but one direction for the motion of the two atoms at the same moment. Also if we had thought the motion of the atoms in circular orbits round the centre of gravity, we should have found the value 2 L_a for the product of the forces directed towards the centre and the space between the atoms.

It is now but natural to assume, that $L_a = \frac{1}{3} L_m$, and in this way to equate the product of the pressure and the space, which is assigned to the motion, for the two cases. Then $\gamma = 1$. And we come the more certainly to this conclusion if we pay attention to what follows.

Let us imagine in the midst of particles moving in all directions, a group which is forced in some way or other to move only in one direction, e. g. in the vertical direction. Let this group be inclosed in a vertical cylinder with mathematic walls. This group could not resist the pressure which is exercised in a horizontal direction, so against the vertical walls — unless we think this group so thin, that the cylinder is but one molecule thick, in which ease the matter of the molecules resists those horizontal pressures. Then the motion has only to resist the pressure on the upper and lower surface, and the product of pressure and volume must be 2 L_a. If now this pressure is equal to the external pressure, brought about by particles moving in all directions, then only the vis viva in vertical direction contributes to that external pressure, which is $^1/_3$ of the total vis viva.

By putting $L_a = \frac{1}{3} L_m$, we bring continuity between the vis viva according to the vertical direction and so the theorem that at given temperature the vis viva of the particles is equally great, is extended also to those components of the vis viva, according to which motion is possible. And just as in co-existing gas- or liquid masses the great internal pressure to which the liquid is subjected, does not disturb the equality of the vis viva, and only influences the degree of density of the substance, in the same way it is not to be expected that the perhaps much greater internal forces which keep the atoms together, influence the equality of the components of the vis viva of the still possible motions, and we have to regard as the only influence of these forces the determination of the dis-

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tance of the atoms. We shall, however, have to apply this with caution. We could easily think, that as two atoms move in the molecule, the vis viva of each molecule would be equal to $^1/_3 L_m$. This conclusion would be inaccurate were it only for the fact that the vis viva of these two atoms is not equal, but that we have the relation:

$$m_1 L_1 = m_2 L_2.$$

We have to regard these two atoms, for which the motion of the one is completely determined by the motion of the other, as one, just as we do not take every half of a particle as a separate whole.

If we put this value of β in $C_{v=\infty} = \frac{3}{2} R(1+\beta) + 3\beta R \frac{T\,db}{(b-b_0)\,dT}$ we find:

$$C_{v=\infty} = R\left[2 + \frac{T}{(b-b_0)}\left(\frac{db}{dT}\right)_{v=\infty}\right].$$

The unknown part which is to be added to $2R$, represents the increase of the potential energy of the atoms. At infinite rarefaction the equation of the equilibrium is simplified to:

$$\frac{dP_b}{db}(b-b_0) = RT.$$

But as by the deduction from the theory of the cyclic motion the case that P_b should be a function of the temperature, is excluded, we find by differentiating logaritmically:

$$\left\{\frac{\frac{d^2P_b}{db^2}}{\frac{dP_b}{db}} + \frac{1}{b-b_0}\right\}\frac{db}{dT} = \frac{1}{T}$$

or

$$\left\{\frac{T\frac{d^2P_b}{db^2}}{\frac{dP_b}{db}} + \frac{T}{(b-b_0)}\right\}\frac{db}{dT} = 1$$

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or

$$\frac{T}{b-b_0}\frac{db}{dT} = 1 - \frac{T\,db}{dT}\frac{\frac{d^2P_b}{db^2}}{\frac{dP_b}{db}}.$$

The supposition that the forces which attract the atoms towards the centre of gravity, are proportionate to the deviation from the shortest distance, would make P_b of the second degree in $b-b_0$, and so $\frac{dP_b}{db}$ of the first degree, and it leads therefore to:

$$\frac{T}{(b-b_0)}\frac{db}{dT} = \frac{1}{2}.$$

With this value we find for a diatomic molecule:

$$C_v = 2^1/_2\, R.$$

As R may be equated to $\frac{1{,}975}{m}$ (m the molecular weight), $C_v = \frac{4{,}94}{m}$.

For C_p we find $3^1/_2\, R$, and we get therefore:

$$\frac{C_p}{C_v} = k = \frac{7}{5} = 1{,}4.$$

For air $C_p = 1{,}4 \cdot \frac{4{,}94}{28{,}8} = 0{,}24$. The value found by REGNAULT is 0,2377. But it is of course very doubtful whether the supposition $P_b = \alpha\,(b-b_0)^2$ is quite correct for all diatomic molecules.

In a following paper we shall have to apply the theory of the cyclic motion also to polyatomic molecules and we shall have to examine what influence this value of b which is variable with the temperature and the pressure has on the equation of state.

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Astronomy. — Report of the Committee for the organisation of the observations of the solar eclipse on May 18th 1901 drawn up by Dr. H. G. VAN DE SANDE BAKHUYZEN.

At the meeting of May 27th 1899 the Academy appointed a committee to organise a Dutch expedition for the observation of the total solar eclipse on May 18th 1901, which will be visible almost exclusively in the Dutch-Indies.

This eclipse is of extraordinary importance because of its long duration, (in the central line on the west coast of Sumatra it will last $6^1/_2$ min. and on the east coast of Borneo $5^1/_2$ min.), so that a great number of accurate observations can be made. The photographic plates will probably show indications of details, of which nothing or only very little has been seen at former eclipses owing to the short time of exposure together with the faintness of the light.

The organisation-committees in Holland and in the Dutch-Indies.

The above mentioned committee appointed by the Academy, from some of its members and other scientific men not belonging to the Academy, consisted of by Messrs. J. A. C. OUDEMANS, J. C. KAPTEYN, W. H. JULIUS, E. F. VAN DE SANDE BAKHUYZEN, J. P. VAN DER STOK, A. A. NYLAND, J. H. WILTERDINK and H. G. VAN DE SANDE BAKHUYZEN. It was very desirable however to assure the co-operation of a committee in the Dutch Indies and in consequence of a correspondence with the Colonial Minister, the Indian Government asked the board of the "Natuurkundige Vereeniging in Nederlandsch-Indië" to take upon them the preparations for the observations. For this purpose the board appointed a committee formed by its President, our corresponding member Major J. J. A. MULLER, R. E. of the Staff, chief of the triangulation in Sumatra, Dr. S. FIGEE, acting-director of the Royal magnetical and meteorological Observatory at Batavia and A. C. ZEEMAN, Inspector of the Governmental navy, and of the beacons, lighthouses and pilotage.

The two committees, always working in collaboration, had a twofold purpose, first to prepare a Dutch expedition for the observation of the important phenomenon, secondly to gather data in order to be able to give information to foreign astronomers who intended to observe the eclipse in India.

Financial support.

A large sum of money was required for the preparation and sen-

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ding out of an eclipse party, not only for the instruments and for the voyage and the maintenance of the observers, but also to enable some members of the expedition to take part in the observations of the total eclipse of May 28th 1900, and to visit some foreign observatories in order to prepare themselves for the task in India.

Already before the committee had been appointed Mr. NYLAND by means of private contributions had collected a considerable sum for this purpose. This sum, though large, was not sufficient and has afterwards been greatly augmented, in the first place by the resolution of the East-Indian Government, which, at the request of the "Koninklijke NatuurkundigeVereeniging in Nederl.-Indië", has allowed the yearly sum on the budget for scientific expeditions, to be used for the Dutch eclipse-party and moreover by the sum which his Excellency the Home-minister had placed at the disposal of the committee in 1900, and which, we expect, will be granted us again this year.

The "Hollandsche Maatschappij der Wetenschappen te Haarlem", the "Provinciaal Utrechtsch Genootschap" and the "Koninklijke Natuurkundige Vereeniging te Batavia", have also sent us considerable contributions, but we are especially glad to record the fact that several private persons, besides those who at the beginning had presented us with large gifts, were ready to give us financial support in the most liberal way.

Another important contribution was received by the committee from the Indian Government, which put at the disposal of the "Koninklijke Natuurkundige Vereeniging" at Batavia 30 copies of 27 maps of differents parts of Sumatra and Borneo. Lastly I have to express my indebtedness to the directors of the steam-navigation company "Nederland", who allowed a reduction in the fares for the members of the expedition and their luggage, and has done much to render the transport of the instruments safer and more convenient.

When it appeared that the financial conditions would allow the sending out of an expedition, one of the chief requirements was to find competent persons to make the observations. The committee was fortunate enough to find two of its members Mr. J. H. WILTERDINK, lecturer of astronomy and observer at Leyden and Professor A. A. NYLAND of Utrecht willing to take this task upon themselves, while Mr. J. J. A. MULLER in India was ready to officiate as chief of the expedition. His scientific abilities and his thorough acquaintance especially of the west part of Sumatra, of which the triangulation was made for the greater part under his direction, ren-

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ders Mr. MULLER's collaboration of great importance for the success of our expedition.

When afterwards it appeared desirable for the spectroscopic and polarimetric work, that a physicist should go with the expedition, we were happy to find the member of our committee Prof. W. H. JULIUS ready to join the party. Mr. MULLER informed us that Captain WACKER at Batavia who has taken part in the triangulation of Sumatra and Dr. FIGEE, acting director and Dr. VAN BEMMELEN acting vice-director of the meteorological observatory will join the Dutch expedition whereby a valuable addition to the observing staff is secured.

In India moreover we hope to avail ourselves of the assistance and collaboration of some officers of the general staff and of the officers and the men of a man of war, which probably, thanks to the kindness of the commander of the navy, will lie during the eclipse in the neighbourhood of the observing station chosen by the committee.

Observations and instruments.

The observations which the members of the expedition expect to make are:

1. Photographs of the corona.
2. Spectroscopic observations of the corona.
3. Spectroscopic observations of the flash in the immediate neighbourhood of the sun.
4. Determinations of the polarisation of several parts of the corona.
5. Determination of the heat radiation from the corona.
6. Determination of the brightness of the corona.
7. Observation of the shadow-bands.
8. Determination of the electrical condition of the air during the eclipse.
9. Determination of the terrestrial magnetism.
10. Observations of temperature, atmospheric pressure and force of the wind.

For these observations the following instruments will be used.

1. *Photographs of the corona.*

As the brightness of the corona at different distances from the

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sun's limb is very different, it is impossible to obtain in the ordinary way a photograph, on which all parts are equally visible. If the image of the corona near the sun's limb shows distinct peculiarities, there will be no visible impression at a greater distance from the sun, and if those more distant portions are visible on the plate, the image of the inner part of the corona will show no detail at all. For this reason it has been resolved to use a number of different photographic cameras: *a*. of great focal length and accordingly with a small value of f/a (f=focal length a=aperture) giving large images of small intensity, and therefore suitable for the reproduction of the inner parts of the corona; *b*. of small focal length and with a great value of f/a giving small but very bright images, and showing the most remote parts of the corona; and finally *c*, a photographic telescope with an arrangement according to BURCKHALTER, where a specially shaped screen rotates with great rapidity directly in front of the sensitive plate and so diminishes artificially the intensity of the light of the coronal portions near the sun's limb. In this way a distinct image of a very great part of the corona may be obtained.

The photographic apparatus are then:

1. A photographic object glass lent by the Observatory at Washington of about 12 m. in focal length and about 11 c. m. in aperture. The proportion f/a is 1 : 92, and the diameter of the image of the sun is about 0.5 c.m.

By means of a light-tight tube of wood and cloth the object glass, firmly mounted on a pillar, is connected with the plate-holder also in a fixed position. A mirror sends the sunlight through the object glass into this telescope.

2. A photographic object glass of STEINHEIL, belonging to the Utrecht observatory, 3,45 m. in focal length and 27 c.m. in aperture; $f/a = 1 : 12{,}8$, giving an image of the sun of 3.2 c.m.

For this object glass an iron tube is constructed, which is fastened to a parallactic mounting from the Leyden Observatory, which by means of a clock follows the diurnal motion of the sun. Three of the above mentioned revolving discs of BURCKHALTER have been constructed after the indications of Mr. NYLAND to be used in conjunction with this object glass (one for each plate), the axes passing through holes in the sensitive plates are rapidly revolving by means of a clock. Mr. NYLAND had also a similar revolving screen of BURCKHALTER made for the long telescope of 12 m. focal length.

3. A photographic object glass of DALLMEYER lent us by "TEYLER's

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Genootschap" 1.52 m. in focal length and 10.8 c.m. in aperture; $f/a = 1/14$ with an image of the sun of 1.4 c.m.

4. A photographic double-lens of VOIGTLÄNDER und SOHN 0.87 m. in focal length and 10.8 c.m. in aperture; $f/a = 1/8$ giving an image of the sun of 8 m.m in diameter.

5. A photographic double-lens of VOIGTLÄNDER 0.38 m. focal length and 10.8 c.m. aperture; $f/a = 1/3.5$, diameter of sun's image 3.5 m.m. For each of the three last object glasses a teak-wooden tube has been constructed, carrying at its other end the wooden plate-holder.

6. An amateur-camera with the back-lens of a collinear object glass of VOIGTLÄNDER, 0.35 m. focal length and 35 m.m. aperture, which probably will be reduced by a stop. The image of the sun is 3.3 m.m. in diameter.

During the observations the four last photographic apparatus will be fastened to a square wooden case, provided at both ends with steel axes running on ball bearings, by which a very smooth motion is obtained. At one end of the case a wooden sector of about 2.7 m. radius has been fixed perpendicularly, and by means of a chord attached to the sector and clockwork, the case with the cameras rotates at the rate of the diurnal motion. If the axis of the case is adjusted in the direction of the polar axis and the cameras have once been pointed to the sun, they will remain in that position.

2 and 3. *Spectroscopic observations.*

For this purpose 4 spectrographs and one visual spectroscope will be used.

One of these spectrographs is a prismatic-camera of COOKE, consisting of an ordinary camera with an object-glass, COOKE's triplet, achromatized both for actinic and visual rays, of 16,2 c.m. aperture and 2.60 m. focal length; in front of the object-glass are placed two prisms with an angle of 45°, covering the whole aperture of the object-glass.

When this apparatus is directed towards the totally eclipsed sun, we obtain on the sensitive plate a series of images of the corona and of the ring immediately surrounding the sun's disc, of the different colours which compose the light of the corona and of the ring.

The dimensions and shapes of these different images, which probably will be very numerous, will show distinctly where the sub-

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stances are situated, whose light forms the pictures on the sensitive plate. Moreover it will be possible to determine the refrangibility of those different kinds of light from the positions of the images although the accuracy of this determination will probably be less than that of the refraction-indices from the measurement of the spectra obtained by means of the slit-spectrographs.

Another spectroscopicinstrument is a slit-spectrograph, constructed by Mr. TOEPFER at Potsdam after the indications of Mr. WILTERDINK in consultation with professor SCHNEIDER of Potsdam.

The lens projecting the image of the sun on the slit is a photographic double-lens of VOIGTLÄNDER of over 10 c.m. aperture and 38 c.m. focal length; two photographic double-lenses of 36 m.m. aperture and 13 c.m. focal length of ZEISS serve as collimator- and cameralenses. The dispersion is obtained with two large Rutherfurd prisms 60×35 m.m. from C. A. STEINHEIL of Munich.

We intend to use this spectrograph for the general corona spectrum and for the spectrum of the upper parts of the photosphere the so-called flash.

By accurate measurements of this corona-spectrum the uncertainty still existing about the refrangibility of the corona light will probably be removed. Moreover we hope to learn from its spectrum something more about the origin of the light of the flash.

The hypothesis, developed by Prof. W. H. JULIUS in his interesting paper read at the meeting of our Academy of February 24th 1900, that this light (flash) may be caused by an abnormal dispersion of the ordinary sunlight, has received new support by the investigations of Prof. WOOD of Wisconsin University. The determination of the refractive-indices of the different lines in the spectrum of this light will probably prove to be an important contribution towards a judgment about this question.

The flash appears immediately after the second contact and as the layer which sends the light to us is thin, it disappears on the central line within one or two seconds. In order to obtain a photographic image of this spectrum, while the calculated moments of its appearance can be several seconds in error, the sensitive plate will be exposed some time before totality begins, and will be slowly moved by a clock, belonging to the Utrecht Observatory, until a few seconds after the second contact. The plate will then show next to each other the ordinary spectrum of the sun and the spectrum of the flash with its bright lines. This juxtaposition of the two spectra has the advantage that the situation of the dark and the bright lines in the two can be easily compared.

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Another slit-spectrograph, also made after Mr. WILTERDINK's design by TOEPFER, has a greater dispersion than the foregoing.

The image of the sun is formed on the slit by a photographic doublet of 8 c.m. aperture and 61 c.m. focal length, while two photographic double-lenses of 5.5 c.m. aperture and 42 c.m. focal length, like the first of VOIGTLÄNDER, served as collimator- and camera-lenses. The dispersion is obtained by three large Rutherfurd prisms made by STEINHEIL 60×55 m.m. We hope that it will be possible to determine with this spectrograph the motion of the particles which make up the corona, by a comparison of the spectra of the corona on both sides of the sun at the place where the greatest velocity of the particles in the direction towards and from the earth is to be expected.

The spectrograph will be pointed so that the centre of the image of the sun falls on the middle of the slit, and as the length of the slit is much greater than the diameter of the sun's image, the spectra of the two parts of the corona situated on both sides of the sun will be obtained on the sensitive plate.

In order to determine the mutual position of the corresponding lines in those two spectra, which on the plate are at a rather large distance from each other, a comparison spectrum of iron will be formed in the intermediate space by electric sparks between a pair of iron electrodes before the slit.

A fourth spectrograph on purpose to still better examine the bright line spectrum of the sun's limb, consists of a plane diffraction grating of ROWLAND, 37×55 m. m., of 14438 lines to the inch; the object glass has an aperture of 62 m. m. and a focal length of 1 m.

This instrument is to be mounted near the limit of the zone of totality, because there the moon's limb at the end of the sun's diameter, perpendicular to the direction of the lunar motion, moves along the sun's limb so that the duration of the flash will be very much prolonged.

Lastly visual observations will be made with a fifth apparatus, namely a slit-spectroscope with great dispersion belonging to the Utrecht Observatory; the condenser is an object-glass of STEINHEIL of 10.8 c. m. aperture, and 0.864 m. focal length.

All this spectroscopic apparatus will be mounted in an approximately horizontal stationary position and the solar light will be reflected into the instruments by means of silvered glass mirrors. As the sun moves on during the observation, the mirrors should move so that during the totality the reflected rays keep a constant direction.

With ROWLAND's diffraction grating this will be obtained by means

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of a coelostat with a mirror of STEINHEIL of 10 8 cm. in diameter, belonging to the Utrecht Observatory; while the prismatic camera, the two slit-spectrographs and the visual spectroscope will be used with siderostats made by GAUTIER of Paris.

These consist each of an axis, mounted in the direction of the polar axis rotating by means of a clock in exactly 24 hours; to each of the ends of this axis a mirror is attached, and this being once adjusted so that it sends the light of a given point of the sun's limb in the direction of the polar axis towards one of the spectroscopic apparatus, the direction of that reflected pencil will remain unchanged.

But it is the direction of this pencil only which is stationary, and which forms a single image, the reflected images of all the other points will rotate very slowly round the image of that fixed point. This slight movement does not influence the spectroscopic observations, but if the reflected image were required for obtaining a picture of the corona, its distinctness would be lessened by the motion.

If a stationary reflected image is desired, as for instance for photographing the corona with the above mentioned horizontally mounted long telescope of 12 m. focal length, the reflection must be brought about in an other way. For this purpose the coelostat of LIPPMANN is very suitable; in this apparatus the mirror, parallel to the polar axis is attached to a metal axis also adjusted in the same direction and rotating once in 48 hours. According to Mr. WILTERDINK's indications GAUTIER has in a simple manner attached such a coelostat to one of his siderostats, and its mirror reflects the sun's rays into the long telescope of 12 meter.

4. *Determination of the polarisation of the corona.*

Prof. JULIUS intends to make a number of polarimetric measurements in order to get to know, for as large a number as possible of well determined places on the corona, the percentage of the polarised light.

For reasons easily to be understood the use of a mirror had to be avoided; therefore a telescope of STEINHEIL-SCHRÖDER (belonging to the Leyden Observatory) equatorially mounted was arranged for these measurements. The object-glass has an aperture of 10.8 c.m. and a focal length of 275 c. m.; the diameter of the moon's image is therefore about 2.5 c.m. During the observation an assistant will keep the central point of the moon's image in the optical axis of the telescope,

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by means of a finder and of a system of rods. Instead of the eye piece a modified polarimeter of CORNU, is attached to the end of the tube so that the diaphragm with a square hole, 1 m.m.^{2}, (of which the polarimeter forms a double image) is situated in the focal plane. The whole polarimeter has two motions, one radially on a slide, so that the diaphragm may come at any desired distance from the axis of the telescope and secondly a rotatory motion round the optical axis of the telescope. The distances radial and angular of each chosen point of the corona can thus be read.

In order to be able to choose those places of the corona most fit for measurements of polarisation, the following arrangement is made: by a quick movement the small diaphragm will be easily removed, and a glassplate put in its place on which an etched square of 1 m. m^2. indicates exactly the spot, which afterwards will be taken up again by the hole in the diaphragm. If the place is chosen, an assistant reads the distance and position angle and the analyser is moved so that both images will have equal brightness. From the position of the analyser the quantity of polarised light may be derived.

The polarimeter with its accessories has been made in the physical laboratory at Utrecht.

Preliminary experiments, made by means of an artificial corona, showed that it will be possible under favourable circumstances to obtain in 6 minutes for at least 12 places of the corona trustworthy values for the ratio of polarised light.

5. *Determination of the radiation from heat of the corona.*

The investigation of the heat radiation from the corona, is also very important for the explanation of this phenomenon, the more so as a great uncertainty still exists, not only about the distribution of this radiation over the spectrum, but also about the question as to the order of magnitude of the total radiation, as appears from the contradictory results obtained on one hand by ABBOTT, on the other by DESLANDRES during the eclipse of May 28, 1900 and later. Prof. JULIUS thought it therefore best to try in the first place to express the amount of radiation of heat from the whole corona in absolute measure, by comparing it directly with the amount of the radiation from the uneclipsed sun, the sun's constant.

For the determination at the eclipse station of the latter radiation a pyrheliometer of KNUT ÅNGSTRÖM of Upsala will be used. Prof. ÅNGSTRÖM has been so kind to test himself the instrument destined for the expedition and to indicate some of its constants.

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The pyrheliometer however is not constructed for very weak radiation, and cannot be used for it. Therefore Mr. JULIUS has made a very sensitive thermopile, which in connection with a resistance-box purposely made for it and a galvanometer of DU BOIS and RUBENS, will enable him to compare amounts of heat-radiation in all ratio's from 1 to 100000.

The thermopile is exposed directly to the radiation without mirrors or lenses, and each time the resistance is so adjusted that the galvanometer gives trustworthy indications. When disturbing influences are eliminated, we may accept without restriction that, when the amount of the radiation is very small, the current is proportional to the absorbed heat.

For strong radiations we can examine by means of the pyrheliometer, in how far the proportion still remains. As the difference in temperature between the junctures of the thermopile, when it is exposed to the sun's radiation in the tropics, will probably not exceed 30° C. it is to be expected that the deviation from the law of proportionality will not be very large; at any rate it can be accounted for. The plan of observation is to repeatedly measure the heat radiation during the whole time of the eclipse, from before the first till after the fourth contact, at well determined moments which comes to us from the sun and its immediate surroundings. The apparatus in which the thermopile is mounted, has been so arranged that the radiation is received only from a circular portion of the sky 3° in diameter.

As long as the radiation of the disappearing or the reappearing disc of the sun is strong enough, observations will also be simultaneously made with the pyrheliometer for testing purposes; it is expected that the thermopile will be able to give indications of the radiation during the whole eclipse. During the totality the apparatus is alternately pointed to the corona and to neighbouring places of the sky outside the corona; from the variations of the galvanometer readings, the amount of the corona radiation will be derived, as a suitable zero cannot be obtained by covering the opening with a screen.

A description of the arrangement of the thermopile and of the elaborate precautions taken to eliminate all disturbing influences, which cause difference of temperature between the junctures, will be given later. Here I record only that in October 1900 on the same day the radiation of the sun and that of the full moon was measured with a provisionarily constructed thermopile and galvanometer, both of which were much less sensitive than the instruments to be used for the eclipse. The radiation of the moon

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falling through a diaphragm (opening 5.5 m.m. in diameter) gave then a deviation of 4.5 divisions, with an error of about 0,5, the proportion of that radiation to the radiation of the sun at noon was found to be 1 : 80000. With the new instruments at least $^1/_{20}$ of the amount of the moon's radiation will be sufficient to make the galvanometer show measurable deviations.

6. *Determination of the light-intensity of the corona.*

It will be possible to derive the relative photographic brightness of the different parts of the corona from the photographs made. But there will be made also observations of the total visual intensity of its light, by means of a photometer of WEBER (comparison with a benzine flame at a variable distance) belonging to the meteorological Observatory at Batavia.

7. *Observation of the shadow-bands.*

The direction and the velocity of these shadow-bands during the eclipse will be determined by observing their motion across horizontal and vertical screens suitably placed.

8. *Determination of the atmospheric electricity.*

An electrometer of the meteorological Observatory at Batavia will register the atmospheric electricity, first on the ordinary rotating cylinder, and then during a period of 6 hours (from 3 hours before till 3 hours after totality) on a cylinder of which the period of rotation is only $^1/_4$ of the former, so that it will be possible to determine the variations during the eclipse with greater accuracy, and to investigate whether the electric potential decreases during the totality.

9. *Terrestrial magnetism.*

The observations of the three elements of terrestrial magnetism will be made at Buitenzorg or Batavia. At Padang the declination and horizontal intensity will be measured by a self-registering ESCHENHAGEN's intensity-variometer and other variation-instruments, to be provided by the observatory at Batavia.

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10. *Determinations of temperature, atmospheric pressure and force of the wind.*

The temperature will be determined by AHSMANN's aspiration thermometers of the Observatory at Batavia, and further by means of a thermograph (large pattern) of RICHARD.

The atmospheric pressure will be determined by ordinary barometers and further by a barograph (large pattern) of RICHARD. The pressure of one millimeter mercury is represented on the scale by 3 millimeters.

The direction and force of the wind will also be determined in order to know whether at this eclipse, as in former cases, a sudden eclipse-wind will be observed.

Selection of the observing station.

For almost all the observations it is necessary that the observing station should be in the neighbourhood of the central line, because there the totality lasts longest and the sun is covered by the moon symmetrically to the direction of its axis. This central line runs from about west to east a few degrees south of the equator. In our East-Indian colonies it passes over Sumatra, a little south of Padang, over Borneo south of Pontianak, and then over Celebes south of the gulf of Tomini, over Boeroe and Ceram and over New Guinea. On the central line the duration of the totality decreases from West to East, at the west coast of Sumatra it lasts 6 min. 30 sec., in New Guinea about 3 min. 30 sec.

Besides the duration of the phenomenon the selection of the astronomical site depends for a great part on the convenience for the transport of the many heavy boxes with instruments, the state of the ground with a view to the mounting of the instruments and on the possibility of getting assistance in the transport and the preparatory work. The examination of these circumstances and the advice to be given accordingly, had to be left to the care of the Indian committee.

For the determination of the weather to be expected, the meteorological Observatory at Batavia could dispose of rain-observations over a long period in a great number of places in our East-Indian colonies and further of general records on the cloudiness in differents parts of the Indian Archipelago.

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But as it was important to know the cloudiness and the duration of the sunshine especially at different points on the line of totality, the meteorological Observatory at Batavia has in twelve places organised observations on the cloudiness and the sunshine during the months April, May and June 1900.

The results of all the meteorological observations, which are important for the selection of the observing station, have been recorded by Mr. J. J. A. MULLER and Dr. S. FIGEE in a paper "Information for observing parties and climatological conditions along the track of the moon's shadow", in which also information is given about the character of the different regions, the means of transport, residence etc., which will have special interest for foreign astronomers, who will go out to observe the eclipse.

The meteorological condition near the equator is on the whole not very favourable; at the several meteorological observing stations hardly any day in May 1900 was perfectly cloudless. But then the clouds do not cover the whole sky, and in the cloudless parts the air is clear and very transparent.

The number of days on which at noon (the moment of the eclipse), the sun was visible near the central line in Sumatra and Borneo, in May 1900 varies from 10 to 30; in most places the number is more than twenty; but it is not allowed to derive general conclusions from these numbers as they represent the results of one month only.

The difference between the meteorological conditions in May 1900 at the different stations was not large, except in a single case.

Perhaps in the interior of Borneo the probability of bright weather is a little greater than in Sumatra, but in Borneo the transport and the mounting of the instruments would give more difficulties.

In order to obtain as much certainty as possible for their report about the most suitable observing station, Messrs. J. J. A. MULLER and S. FIGEE visited many places in Sumatra from 16th September to 1st October 1900. As the result of their considerations they have recommended to us for our observing station a place in the neighbourhood of PAINAN, on the West-coast of Sumatra, south of Padang; and for the present this point has been chosen as the station of the expedition.

It offers the advantage of being in the neighbourhood of Padang, the seat of the government of the West-coast of Sumatra and the residence of the director of the railway in Sumatra and of the workshops belonging to it, of which much use can be derived for the arrangements of the observing camp.

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Information for the observers of the eclipse.

As I have mentioned already, one of the purposes of our committee was to give information to persons who wanted to observe the eclipse in India, in the first place to foreign astronomers. And it is especially for them that Messrs. MULLER and FIGEE have published the above mentioned "Informations etc.", which have been sent by them and by the Dutch committee to those societies and astronomers who were thought to have an interest in them.

As I have mentioned we have received from the "Koninklijke Natuurkundige Vereeniging" at Batavia 30 copies of 27 maps chiefly of different parts of Sumatra and Borneo, put at their disposal by the Indian government.

We have distributed a great number of those maps among the astronomers who intend to observe the eclipse, so that they will be able to find their way in the stations they have selected. When these astronomers apply to the local authorities on their arrival in India, they will there obtain any assistance and information they require.

The following foreign expeditions, as far as we know, will go to the Dutch Indies :

1. Mr. NEWALL from Cambridge and Mr. DYSON from Greenwich.
2. Mr. LOCKYER from London.
3. Count DE LA BAUME PLUVINEL from Paris.
4. A Russian expedition.
5. Prof. BARNARD from Yerkes Observatory near Chicago.
6. Prof SKINNER from the U. S. Naval Observatory in Washington.
7. Prof. JEWELL from the John Hopkins University.
8. Prof. BURCKHALTER from California.
9. Prof. PERRINE with some assistants from Lick-Observatory.
10. An expedition from the technological Institute of Boston.
11. Mr. TODD from Amherst Observatory.

Probably still other English observers will join these.

Besides the information mentioned, especially for the use of astronomers, some members of the committee have given a list of instructions for eclipse work for amateurs not provided with great astronomical instruments. These instructions were sent to India some time ago.

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At the end of this report the committee would like to express their indebtedness to all who have helped them in their task and have enabled them to send out the expedition.

To His Excellency the Home minister, the "Hollandsche Maatschappij der Wetenschappen", the "Provinciaal Utrechtsch Genootschap", the "Koninklijke Natuurkundige Vereeniging" at Batavia, and especially to the various persons who have given financial support.

To His Excellency the Colonial Minister, who has supported our requests to the Indian government; to the Indian government itself who not only gave us a considerable contribution, but who also enabled Messrs. MULLER and FIGEE to make the above-mentioned expedition in September 1900, and allowed them and other Officers of the General Staff and of the Observatory at Batavia to join the expedition, and who in May will send a man of war to Padang, of which the officers and men will assist in the observation of the eclipse. Our last but not our least thanks is due to the East-Indian eclipse committee, who have taken every pain and trouble to prepare things in such an excellent way in India.

After this report was written tidings are received that according to a royal decree of February 16th 1901 N°. 33 Dr. W. H. JULIUS and Dr. A. A. NYLAND, professors at the University of Utrecht and Mr. J. H. WILTERDINK lecturer and observer at the University of Leyden are charged to go to India with a view to the university interest, in order to observe the total eclipse on 18th May 1901.

This new proof of the interest shown by our government in this expedition is received with much thanks.

(March 22, 1901).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 30, 1901.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 Maart 1901, Dl. IX).

CONTENTS: J. H. BONNEMA: "On the occurrence of remains of Leperditia grandis SCHRENCK sp. in the erratic blocks of the Groningen diluvium" (Communicated by Prof. J. W. MOLL), p. 545. — Prof. J. A. C. OUDEMANS: "On the contents of the sixth and last part of the Report "Die Triangulation von Java", p. 549 (with one plate). — Dr. ERNST COHEN and E. H. BUCHNER: "ETARD's law of solubility (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM) p. 561. — Prof. J. C. KLUYVER: "On the expansion of a function in a series of polynomials", p. 565. — Prof. J. D. VAN DER WAALS: "The equation of state and the theory of cyclic motion" II, p. 571. — J. BRAND: "Researches on the secretion and composition of bile in living men", (Communicated by Prof. B. J. STOKVIS) p. 584. — Prof. M. W. BEIJERINCK: "On oligonitrophilous Bacteria" p. 586. — Dr. C. H. WIND: "On the irregularities of the cadmium standard cell", (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM) p. 595. — S. L. SCHOUTEN: "A pure culture of Saprolegniaceae", (Communicated by Prof. F. A. F. C. WENT) p. 601.

The following papers were read:

Geology. — J. H. BONNEMA, at Leeuwarden: "*On the occurrence of remains of Leperditia grandis* SCHRENCK *sp. in the erratic blocks of the Groningen diluvium.*" (Communicated by Prof. J. W. MOLL).

(Read November 24, 1900).

1852. *Cypridina grandis* A. SCHRENCK. Survey of the upper silurian shaft-system in Livonia, Esth- and Kurland. Dorp. Archives, Series I, Vol. I, p. 58.

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1858. *Leperditia Baltica* Fr. von Schmidt. Researches into the silurian formation of Esthland, North Livonia and Oesel. Dorp. Archives, Series I, Vol. 2nd, p. 171 and 192 (ex parte).

1858. *Leperditia gigantea* F. Roemer. On a gigantic species of the genus Leperditia. Journal of the German Geological society Vol. 10th, p. 356.

1859. *Leperditia grandis* Fr. von Schmidt. Some communications on the geognostic condition of the Isle of Gothland. Dorp. Arch. Series I, Vol. 2nd, p. 455.

1860. *Leperditia grandis* Eichwald. Leth. ross. anc. per. page 1332, plate 51, fig. 9, *a*, *b*, *c*.

1872. *Leperditia gigantea* J. Barrande. Supplement to Vol. I, on the silurian system of central Bohemia, page 535, plate 34, fig. 4, 5, 6.

1873. *Leperditia grandis* Fr. von Schmidt. Miscellanea Silurica I. On the Russian silurian Leperditiae, Academ. Memoirs St. Petersburg, Vol. XXI, No. 2, page 10, fig. 3, 4, 5, 6.

1876. *Leperditia (Isochilina) gigantea* F. Roemer. Leth. pal. Atlas, plate 19, fig. 8.

1879. *Leperditia grandis* Kolmodin. Ostracoda silurica Gotlandiae. Scientific Acad. treatise. N°. 9, page 135.

1881. *Isochilina grandis* Jones. Some Cambrian and silurian Leperditiae and Primitiae. Ann. and Mag. Nat. Hist. series 5th, Vol. 8th, page 347.

1882. *Leperditia grandis* Fr. v. Schmidt and Jones. On some silurian Leperditiae, Ann. and Mag. Nat. Hist. series 5th, Vol. 9th, page 169.

1882. *Leperditia grandis* Nötling. The Cambric and silurian erratic blocks of East- and West-Prussia. Annals of the Prussian, geol. government Institution, p. 295. (Preuss. geol. Landesanstalt.)

1883. *Leperditia grandis* Fr. von Schmidt. Miscellanea Silurica III. Sequel to the Russian Silur. Leperditiae, Academ. Memoirs. St. Petersburg, series VII, Vol. XXXI, N°. 5, page 8.

1884. *Leperditia gigantea* F. Roemer. Leth. errat. page 84.

1891. *Leperditia gigantea* Krause. The Ostracoda of the sil. diluvian erratic blocks. Scientific supplement Program of the Luisenstädtischen Oberrealschule at Berlin (a first-class High-school, a town institution).

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One of the most remarkable phenomena, I observed, when studying the sedimentary boulders of the Groningen Hondsrug, I consider to be, the repeated occurrence of limestone, with remains of Leperditia grandis SCHRENCK sp. For of this interesting Lep. species twenty-two, more or less intact valves, of different sizes, are kept in the Geol. Museum of the Groningen University, among the collection: "Groningen Erratic Blocks"; the specimens found still outnumbering those of the collection.

That large number is rather remarkable, considering that in the whole of Germany, only three specimens have been found, i. e. in East Prussia, one at Lyck, and two in the neighbourhood of Koningsbergen.

Up to now no statement has been made of a single specimen having been found in the whole stretch of land, between East Prussia and Groningen.

Leperditia grandis SCHRENCK sp., can be easily recognised, both for its dimension and for its morphological characteristics. As the name indicates, it may attain to an extraordinary size, for Leperditia. So e.g. the largest valve (a right one) that has been found at Groningen, has a hinge-line, 20 m.m. long, whereas the largest valve of the other Leperditia species, found there, has a hinge-line of 15 m.m. It is a right valve of Leperditia Baltica His sp. The eye-tubercles are very strongly developed. The ventral border is nearly straight, and gradually slopes up from the back to the front. The greatest thickness (distance from one valve to the other) is found close to the ventral border and diminishes parallel with it.

Both valves have behind the eye-tubercle a groove (sulcus), which from the central spot runs vertically up to the dorsal margin.

At the anterior and posterior borders both valves present a wide, depressed margin.

The right valve has a round opening in the places where those marginal rims end.

The left valve behind the sulcus, which from the central spot runs up to the dorsal margin, has bulged out in growing, a thing which is most distinctly to be seen in the oldest specimens.

Only in the middle of the ventral border, this valve has a little developed inverted ventral plate.

The species of stone, in which by far most remains of these Leperditae have been found, may be easily recognised.

It is a sort of close grained slivery limestone, of a light grey, some times greenish colour.

Through corroding, it turns more yellowish grey.

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Through it run, in crystalline calc. spars, petrified coral trees of the species called Laceripora Cribosa EICHW.

In this stone-formation, besides Leperditia grandis SCHRENCK sp. and Laceripora cribrosa EICHW. sp.: Iliona prisca His, and Merestina didyma Dalm sp., have been found.

The very nature of this species of stone, renders it, as a rule, difficult, to get the specimens out uhdamaged.

There is greater possibility of success, when they are embedded in layers of a softer substance, which one now and then comes across. Much rarer than in the above mentioned slivery light grey limestone, remains of Leperditia grandis occur in fine-grained, more brownish limestone, which also contains coral trees of Lacipora cribosa.

Remains of Leperditia phaseolus His. sp. and of Proetus conspersus Ang. are also found in it.

As to their age, both sorts of limestone, must be ranked with the Upper-Oesel layer and more especially, with the yellow zone of it.

This sufficiently appears from the fossils, they contain.

To conclude, there remains to be traced whether such like stone-formations are still known to exist as compact rocky masses.

Limestone, with remains of Leperditia grandis, is found in a compact rockey mass, in Gothland and in Oesel. In the first mentioned island, near Ratthammersvik. According to VON SCHMIDT (Researches etc. page 171) it occurs in Oesel, in a quarry, not far from the "Ticko-Krug", near Hoheneichen and in another one near Lümmada, in a wood on the road to Arensburg.

When travelling through those parts, which I had the honour of doing under the mentorship of VON SCHMIDT, I collected two pieces of limestone, which contain remains of Leperditia grandis according to the labels, named to me by VON SCHMIDT, the one comes from the quarry at Lümmada, the other from the one at Puzza. The latter find-place being no doubt the same, VON SCHMIDT l. c. states to be the one near the Ticko-Krug. The Groningen erratica differs from the piece found at Lümmada.

Some light-grey, slivery pieces however, petrographically, perfectly resemble the stone-formation of Puzza. Still, they are not altogether alike, the valves of Leperditia grandis, which occur in the Groningen erratica, in size, remaining considerably below those found in the stone-formation of Puzza. According to VON SCHMIDT, (Miscellanea Silurica III, page 9), the valves of Leperditia grandis in Gothland are, as a rule, smaller than those in Oesel; so in this respect the Groningen erratica which are the subject of this paper show resemblance with the Katthammersvik stone-formation.

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Whether they do so also petrographically, I cannot decide, having no specimens of the last mentioned place to compare them with. So I cannot ascertain whether, and if so, where, limestone, with remains of Leperditia grandis, found in the Groningen diluvium, still exists in a compact rocky mass. —

Geodesy. — On the contents of the sixth and last part of the Report "die Triangulation von Java", lately presented to the Academy, in the name of the Netherlands Government, by Prof. J. A. C. OUDEMANS.

(Read February 23, 1900).

As I had the honour to state at the meeting of January 2, 1897, the fifth part of this Report contains the complete results of the triangulation of Java, primary and secondary [1]). It contains the length in metres and the azimuths at both ends of every side of the triangles. Finally a table exhibits the geodetic longitudes and latitudes of all the stations, as they were calculated, starting from the station Genoek in the Residency of Djepara, where the late Geographical Engineer SOETERS made an accurate astronomical determination of latitude and azimuth; the same table contains also the heights above the mean level of the sea, (see IV Abth., p. 206, line 4 from the bottom.)

How these heights were obtained had hitherto not been explained; it is done in the now completed 6th part.

I beg to communicate in a few words some particulars about these calculations. At any station near the seaboard the height above the mean sea level can be measured directly, taking as far as possible the tides into account. This was done for 19 stations, 8 primary and 11 secondary ones, and these were the starting points for obtaining the heights of the stations situated further inland, but for the last a knowledge of the refraction is required.

Owing to the diminution, of the density of the atmosphere with increasing elevation, a ray of light traversing it in a nearly horizontal direction is bent downwards.

Now if at one station be measured the zenith distance of

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[1]) The primary triangulation was already treated of in the 4th part, but the results were reprinted in the 5th.

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another, whose distance is known, the difference of height may be calculated, provided the mean radius of curvature of the ray of light between the two stations be known. If that radius be n times that of the earth's surface between the two stations, $\frac{1}{n}$ is generally called the coefficient of terrestrial refraction, and its half, which is used in the calculation of the difference of height, if the path of the ray is supposed to be circular, will here be called the *factor of refraction* [1]).

This factor may be found, either, as BAUERNFEIND did in Bavaria, by measuring the zenith distance of a distant station, whose height above the observing station has been accurately determined by spirit levelling — or by measuring, at each station, the zenith distance of the other. Both these methods, especially the latter, have been repeatedly applied, but the results were very discordant. Theoretically the factor is known to depend on the indications of barometer and thermometer, but still more, nay principally, on the law of diminution of the density of the air with increasing height.

As this law was unknown for Java, and as the factor was suspected to be very variable, being dependent on the time of the day and on atmospheric conditions, the design was long ago formed in the Geographical Service to make a special determination of this factor, by reciprocal and simultaneous observations of zenith distances at different hours of the day. This design has been carried out since I left Java, under the direction of the late engineers WOLDRINGH and SOETERS.

In 1876 Engineer WOLDRINGH made two determinations, assisted by Assistant JACQUES OUDEMANS. On one day the reciprocal zenith distances were simultaneously measured five times between the south end of the Simplak base and the summit of the Salak, and shortly afterwards three times between the same base end and the station Tjitjadas; the difference of height being 2015 metres in the first, and only 44 metres in the last case. (The heights above sea level were: base end 195, Salak 2210, Tjitjadas 235 metres). The results were different, and in the last named determination there existed from half past seven till half past ten a. m. a considerable diminution of the value of the factor of refraction. This led to the arrangement of systematic series of observations. A first series

[1]) In Clark's Geodesy, the half of $\frac{1}{n}$, which we call the factor, is called the coefficient of refraction.

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was observed between the stations Banjoepahit, Penoenggalan and Basé in Middle Java, by Messrs SOETERS, JACQUES OUDEMANS and DE VLETTER. Unhappily the observations of the last named observer are lost; perhaps this is the reason, why the same observers performed new series between three other summits in East Java, viz. in March and April 1878 between the stations Djoerangsapi, Poetri and Tanahwoelan, and in November of the same year between Petjaloengan, Poetri and Tanahwoelan. (The heights were: Djoerangsapi 230, Poetri 976, Tanahwoelan 761, Petjaloengan 534 metres).

Between each pair of stations the zenith distances were repeatedly measured strictly simultaneously, e.g. at 8 h. between the first and second, at 8 h. 20 m. between the first and third, at 8 h. 40 m. between the second and third station, and so on. The observations were commenced early in the morning and continued as long as rising clouds did not interfere.

The general conclusion from these researches was, that the factor of refraction diminished from early in the morning till noon, at first rapidly, and afterwards more slowly; of course this is easily explained by the rising of the heated inferior layers of air.

But a remarkable result was, that each pair of stations gave a different value for the factor of refraction; thus, while in March 1877 Penoenggalan and Banjoepahit gave for the mean 0,0547, (minimum at noon 0,0510,) the mean result from Petjaloengan and Poetri was 0,0882, (maximum at 8 h. 0,0973).

It was thought that these differences could be accounted for by deviations of the plumbline, caused by local attractions; for such attractions displace the zeniths and so alter the zenith distances; but the attempt to explain the observed differences in this way, proved unsuccessful; at least it would have been necessary to assume very large deviations of the plumbline, different in sign, besides as has been already stated, in March and April of 1878 the observations were made at Tanahwoelan, Poetri and *Djoerangsapi*, and in November of the same year at Tanahwoelan, Poetri and *Petjaloengan*; now the deviations of the plumblines at Tanahwoelan and Poetri, needed to render concordant the observations of March and April, did not agree, either in direction or magnitude, with those which would have harmonized the observations of November. Attempts to explain the variations of the factor of refraction by the indications of barometer and thermometer, were equally unsuccessful and it seemed necessary to conclude that the layers of air of equal density are by no means parallel to the spherical or ellipsoidal surface of the earth, but that they follow the sinuosities

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of the ground, so that every pair of mountaintops or rather of stations has its own factor of refraction.

As it was nevertheless desired to obtain a mean factor of refraction, my zealous coadjutor, Coronel M. L. J. VAN ASPEREN, late of the R. D. N., who had executed most of these calculations, proposed to me to select all the pairs of stations between which reciprocal zenith distances had been observed, whether simultaneously or not. In this research East and West Java were kept separated, but they gave very nearly the same result, namely 0,068. In all there were 114 results, ranging from 0,0392 to 0,0879.

These 114 values were then divided and ranged in 11 groups, in three different ways; 1st. according to distances, varying from 23,9 to 69,5 kilometres; 2nd. according to mean heights, ranging from 123 to 2673 metres, and 3rd. according to zenith distances, taking for each pair of stations the arithmetical mean between the smaller zenith distance and the supplement of the other.

My reason for arranging the results according to distances, was that in the triangulation of Hanover, GAUSS found the factor of refraction to be dependent on the distance between the stations, the greater distances giving a larger factor, but this was easily explained by the flatness of the country.

Between two stations that were not far apart, the ray of light almost grazed the surface of the ground, and it is a known fact, that in this case, by the heating of the soil and the so caused diminution of density of the undermost layers of the air, the factor of refraction often diminishes, and not seldom becomes negative, in which case the convex instead of the concave side of the ray of light is turned to the earth. Of course in Hanover great distances were only to be found between relatively high summits, and so the ray of light between such stations was often free from this influence.

In Java no influence either of distance or of zenith distance on the refraction was remarked. As regards mean height, its increase was accompanied by a feeble diminution of the factor of refraction, but not until the mean height amounted to 2000 metres. For this reason the theoretical diminution of the factor with increasing height has been ignored.

As we now came to deduce the differences of heights from the zenith distances, and to calculate from these, in connection with the heights measured directly at the seaboards, the heights of the inland stations above sea level, it seemed proper to use the 114 cases, in which, as above stated, reciprocal zenith distances were observed, but not simultaneously; in such cases the difference of height may

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be calculated by a known formula [1]), not involving the factor of refraction.

For calculating the remaining differences of height the value of the factor of refraction had to be taken into account. Fortunately its influence on the shorter sides of the secondary triangulation was always small; very often a method was used which had the advantage of diminishing considerably the influence of abnormal refraction, viz: measuring the zenith distances of both the stations from a third station simultaneously, or at least the one immediately after the other.

As the general rule was, to measure from every station zenith distances of all the surrounding stations, there were many more given quantities than were necessary to determine the heights of all the stations, primary as well as secondary; so the differences of height had to be deduced by the method of least squares; but as the stations were too numerous to be all included in one solution, it was necessary to combine them in groups. The manner in which the division of the work took place is clearly indicated by a map printed in colours, of which I give a pair of reprints to circulate [2]).

As already mentioned, the heights of all stations near the seaboard were measured directly, the heights of the other stations being derived from these. The heights given in the Report are those of the tops of the triangulation pillars, generally built up 1,1 metre above the ground, upon a foundation of one meter depth.

In the deduction of the most probable values the weights of the measured differences of height were taken into account; it was therefore necessary to distinguish between the three ways in which these differences had been found, viz. by measuring from one of the two stations concerned or from both reciprocally, or from a third station. The report gives these particulars. In the primary work reciprocal zenith distances were almost exclusively used.

After the heights of the primary stations had been fixed, the heights of the secondary stations were deduced, taking into account the weights of the several determinations.

The result of an elaborate examination was, that the average mean error of a deduced difference of height was about half a metre.

I also computed the mean error (in seconds) of a single zenith

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[1]) Viz. the formula: $h' - h = S\left(1 + \frac{h'+h}{2R}\right) tg\, \frac{1}{2}\,(z' - z)$.

[2]) Plate III of the Report. As the stones, that have served for this plate, as also for the plates I and II, have been ground out, it has been impossible to join them to the printed abstract.

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distance, such as had been used in determining the differences in height. The result found was ± 9″,6, whereas the mean error of the reciprocal simultaneous observations was only ± 2″,2. The inference is, that, if we wish to find the accurate difference in height between two stations, between which the ground is too hilly for spirit levelling, *simultaneous reciprocal* zenith distances ought exclusively to be taken.

In Java the determination of the heights was of quite secondary interest, and the results (which were confirmed by further researches) were sufficient for the purposes of the Survey; but at other times and in other regions there have been cases, where the difference of height was the chief aim, and this rule was not observed.

In the operations executed in 1825, under the direction of colonel CORABOEUF, for the geodetic determination of the difference of height between the Atlantic and the Mediterranean, every care was bestowed on the triangulation of the summits of the Pyrenees; the zenith distances too were often repeated, three or five series, each consisting of ten observations, being taken on each occasion; but the reciprocal zenith distances were not observed simultaneously, though the double staff rendered it practicable. The result might have been more satisfactory, if this precaution had been taken, but it must be allowed that at that time attention had not yet been drawn to the point.

A separate chapter of the Report is consecrated to the dip of the horizon, observed at 53 stations. It soon appeared that these observations could not compete with those already mentioned for determining the heights above mean sea level; they have accordingly not been used for this purpose.

But it was quite another thing, being given the already fixed heights of those 53 stations and the observed dips, to deduce *a posteriori* a formula by which the height above the sea might be calculated from the dip.

This problem also initiated several inquiries. The height is best calculated by a series containing the even powers of $tg\,d$. Now, in trying to determine, by the observed dips, the coefficient of $tg^2\,d$, (on which the 5½ times smaller one of $tg^4 d$ depends), the computed heights of the low stations were generally too great, a result easily explained by the already mentioned inversion of the curvature of the ray of light near the level of the sea. Indeed, following a ray of light from the sea to a distant mountaintop and supposing a point of inflexion to occur near the sea level, then it is easy to see, that in determining the height of any point on the ray by the dip, the

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error made will be the same for all points on the ray. Indeed, as a diagram immediately shows, this error is equal to the linear quantity by which that part of the ray of light, which is concave on the side turned to the earth, dips under the level of the sea, if prolonged at the sea-end.

By the method of least squares, it was easy to find this so called constant, as well as the coefficient of $tg^2\, d$, and thence the factor of refraction.

The first step was to take the arithmetical mean of all the dips observed at the same station; the second term, containing $tg^4 d$, proved small enough to be neglected if the height did not exceed 2000 metres; and so the problem was reduced to the solving of 53 equations with 2 unknown quantities. The coefficient of $tg^2 d$ being thus determined, the factor of refraction was calculated [1]), and agreed almost perfectly with the value found before; finally the coefficient of $tg^4 d$ was deduced. The result was

$$h = (6{,}56546)\, tg^2 d - (5{,}82716)\, tg^4 d - 2{,}475,$$

h being in metres, and the numbers in the brackets being logarithms of the actual coefficients. The value of the factor of refraction, deduced from the first coefficient, is 0,0692, whereas the reciprocal zenith distances gave 0,068. Considering the diverging values that are found for this number, the agreement is more than sufficient.

The same material, however, seemed to invite a more detailed inquiry. Often, at the same station, the dip has been observed at different hours of the day, and it seemed to be worth while to examine the changes of the factor of refraction during the hours of observation. The result is shown graphically on plate II. At 11 a. m. both methods give nearly the same value, viz. 0,0680; before and after, the dips give a smaller value than the reciprocal zenith distances.

The same plate shows in a little map at the bottom, all the stations where the dip has been observed. They appear to be very regularly distributed along the south coast of Java and in the eastern part of the north coast; we also see that the dips were observed in different azimuths. Now, as the radius of curvature of the earth, (or of the ocean), differs with the azimuth, it is

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[1]) Calling the coefficient of $tg^2 d$ a, the factor of refraction k and the radius of the earth R, we have $a = \frac{R}{2-4k}$, or $k = \frac{1}{2} - \frac{R}{4a}$.

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necessary, if we wish to calculate with precision, to take this into account and to reduce the observed dips (for instance) to dips belonging to a mean radius of curvature.

I was sorry not to be able to take the tides into consideration, though they have been thoroughly investigated[1]), for a great number of stations, by our honoured Correspondent Dr. J. P. VAN DER STOK, who embodied his results in tide tables. But these tables commence with the year 1891, and it would have been a laborious operation to extend them to the period containing the observations (1865—1880) and to deduce, by the cotidal lines, (also drawn by the same author), the height of the sea at the moments of the observations.

In most cases neither the azimuth was noted, nor the hour of the observation; and it was necessary to make assumptions with regard to both; as to the azimuth, the dip observation was supposed to be made in a direction perpendicular to the coast line; as to the hour of observation, it was supposed that the horizontal observations commenced at half past six, and that every observation, horizontal or vertical, occupied five minutes. This gave the time of the dip observation.

This investigation led me to frame the following rules for future observations of dip.

1. At every observation the apparent time is to be noted, as also the indications of barometer, thermometer and psychrometer.

2. Repeating the observations on several days is recommended, in order to neutralize accidental deviations and to discover extraordinary perturbations.

3. It is useful to take the measures in different azimuths, especially, if possible, in the meridian and in a direction perpendicular to the meridian, in order to examine whether the theoretically existing difference of the dips in these two directions, which may amount to one part in 150, or to 24″ in a dip of one degree, is confirmed by experience.

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1) These researches have been published in fifteen papers; 13 of these in the "Tijdschrift van het Koninklijk Instituut van Ingenieurs, Afdeeling Ned. Indië, 1890—1896". The title of the first paper, translated, is "The Harmonic Analysis of Tides, applied to Observations made at Tjilatjap"; that of all the following: "Studies of the Tides in the Indian Archipelago"; II and III contain theoretical matter, IV—XIII the results of the harmonic analysis, applied to the indications of the tide gauges established in different parts of the East-Indian Archipelago. XIV (Statistics) and XV (Predictions) have been published in the Journal of the Royal Physical Society of Batavia, Vol. LVI, 1896.

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4. The stations are to be so chosen, that the height of the tide may be calculated by the tide-tables.

I have thought that a review of previous investigations of terrestrial refraction, would not be unwelcome to those interested in the subject. It includes an account of the work of JEAN DOMINIQUE CASSINI in 1661, CESAR FRANÇOIS CASSINI in 1742, TOBIAS MAYER in 1751, LAMBERT in 1759, BOUGUER in 1749, ROY and MUDGE from 1787 to 1799, MÉCHAIN and DELAMBRE from 1792 to 1797, VON ZACH in 1795, WARREN in 1804, VON LINDENAU in 1805, TRALLES in 1806, GAUSS in 1823, WILHELM STRUVE in 1826—27, CORABOEUF in 1827, CACCIATORE in 1831, BESSEL in 1834, BAEYER in 1835, SABLER and STRUVE in 1838, ATKINSON in 1825, DENZLER in 1842, PILAAR in 1846. Then follows a description of the theories of LAPLACE, BAEYER, BABINET, SAWITSCH, BAUERNFEIND, LINDHAGEN, HELMERT, JORDAN and WALTER. The chapter closes by mentioning the value of the factor of refraction which on my suggestion Coronel M. L. J. VAN ASPEREN has deduced from the observations of the Peruvian Committee for measuring a degree in Peru in 1735, and finally by summing up a number of papers on terrestrial refraction, published since 1850 in different periodicals.

The second section of this sixth part contains the determinations of latitudes and differences of longitude, made for comparison with the results of the triangulation, with a view to detecting deviations of the plumbline by local attraction.

Determinations of latitude by circummeridian zenith distances were made at 63 stations. For reducing these observations the knowledge of the declinations of the stars employed was requisite; and though most of the stars were taken from the Nautical Almanac, whose places for the northern stars rest almost exclusively on observations made at Greenwich, it was thought desirable to take into account some other determinations, especially as the declinations of those southern stars which could not be observed at Greenwich were very uncertain.

For the determinations of azimuths made, (in absence of our Pole star), by KAISER's method, by measuring the difference in azimuth between stars in the east or west and some visible station, the precise knowledge of the declinations of the observed stars was also of much interest; sometimes stars were employed for the azimuths which had also served for latitude, yet the choice of stars was guided by different considerations in the two cases and stars

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fit for the determination of latitude, were not always appropriate for that of the azimuth [1]).

The late Dr. N. M. KAM, whose catalogue of stars is well known, undertook, at my request, to furnish a list of the declinations of the stars employed; the numerous star catalogues which he had to consult being forwarded to him from the library of the Utrecht Observatory. He carried out this task very thoroughly, including corrections for the systematic differences of the catalogues. I must add, that when KAM undertook this work, it was not known that AUWERS, of Berlin, was about to undertake a similar one.

Neither for the determination of the latitudes, nor of the azimuths, was it deemed necessary to submit the right ascensions to an equally severe examination. In the determination of latitude a small error in the R. A. was entirely eliminated by the circummeridian observations; in the determinations of the azimuths, which were made for 20 stations, the influence of such an error was always either 0, or so small that the Right Ascensions could be taken directly from the Nautical Almanac.

That a careful determination of the declinations was not without utility, may be shown by the following instances: the correction of the declination of α Andromedae in the Nautical Almanac for 1854 was $-$ 0″,86, in that of 1871 $+$ 0″,03; that of the declination of γ Pegasi was $+$ 0″,7 in 1876, 78 and 79; that of ε Leporis, from 1871 to 1880, was nearly a second; that of the declination of Sirius varied from $+$ 1″,30 to $-$ 1″,89, that of the declination of Procyon from $-$ 0″,55 to $+$ 1″,58, and so on.

Dr. KAM also charged himself with the deduction of the definitive

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[1]) For the determination of a latitude generally stars were employed (commonly four on the north and four on the south,) that culminated at 20° or more from the zenith; the rule was to choose them so that the sums of the zenith distances on the two sides of the zenith were nearly equal; whereas for the determination of an azimuth, the stars ought to be so chosen that at a low altitude their azimuths changed as little as possible. Therefore KAISER, in his "Treatise on the astronomical determination of geographical positions in the East Indian Archipelago" proposed to choose, for this purpose, stars, which, having an altitude of from 10° to 30°, were either in the east or in the west.

Those stars were of course preferable, that moved vertically; (astronomically: whose parallactic angle was 90°:) which was only possible if the star's southern declination exceeded the latitude of the station; but even if the star be not in this most favorable situation, still, provided it stands not higher than 30°, a possible uncertainty of the time, as well as of the latitude, has only a very small influence on the azimuth.

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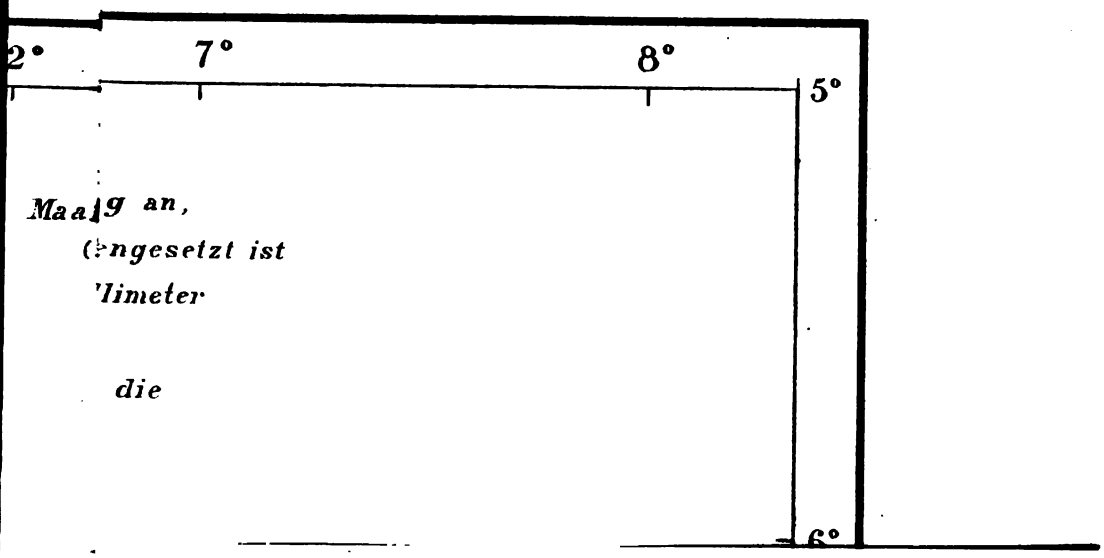

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latitudes and azimuths, taking into account the flexure of the telescope[1]).

All these determinations of latitude were made for the purpose of finding the differences between the astronomical and geodetic latitudes, due to deviations of the direction of gravity from the normal to the adopted ellipsoidal surface, on which the whole network of triangles is supposed to be projected. In German these differences are called "*Lothabweichungen*"; I think an unequivocal Dutch expression would be: "*afwijking van het paslood*" or "*pasloodafwijking*". It may arise *either* from the stronger attraction of mountains or heavy underground masses, *or* from the feebler attraction of less heavy masses on the opposite side. Which cause is the true one in any particular instance, may be decided with more or less probability by measuring the force of attraction by pendulum experiments.

The deviations are represented on plate IV[2]) by arrows, directed to the north or to the south, according to the direction of the attraction. It must be kept in mind, that if the arrow points to the north, the astronomical observations indicate a greater (meridional) latitude then the geodetical ones.

Though attraction by the mountainous country is undeniably indicated, the arrows on the south coast being all directed to the north, and those on the north coast almost all to the south, yet some decided irregularities may be noticed. Though, for instance, seven stations, situated within or near to the Residency of Semarang, indicate an attraction to the south, we find at Genoek, near the north point of Djepara, very little or no attraction, notwithstanding the vicinity of the mountain Moeria. Again, while several stations situated on the north coast, Anjer, Gedé, Batavia, Pakis, Indramajoe, Boetak (in the Residency of Rembang), show an absence of attraction, which might have been expected from their great distance from high mountains, the enormous deviations, 37" in Poelo Tindjil and 26",5 in Pogor II, both near the south coast, are very remarkable. An explanation, however, of this phenomenon may be found, not in the attraction of a high mountain on the north, but in the lack of

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[1]) Dr. KAM examined also, at my request, the changes that would result in these latitudes, (*A*,) if the flexure of the telescope was not calculated for each night separately, but its mean value for the whole period was employed; (*B*,) if the flexure was simply put $= 0$, so that the arithmetical mean of all the determinations was adopted as the definitive value of the latitude.

The result was, that, owing to the suitable choice of the stars on both sides of the zenith, the differences were extremely small, and in the great majority of cases did not reach a tenth of a second.

[2]) As the stone, on which this plate was engraved, was not yet ground out, it has been appended to this abstract.

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attraction to the south by the deep Indian Ocean. The southward attraction at Patjarloewong is strange, there being no remarkable mountain to the south of this station, and the near lying Pliken showing already clearly the attraction of the Slamat on the north east. We are also struck by the southward arrow at Magetan, which has the mighty Lawoe rising near it on the northwest.

Other remarks could be made with regard to the directions and lengths of the arrows on this map, but I think these are sufficient At all events I think the conclusion is evident, that the deviations of the plumbline, detected by the determinations of latitude, show the desirability of a much larger number of such determinations. If we wish to combine the study of plumbline deviations with triangulation, it is desirable to make a determination of latitude at every station; it is then not necessary to attain a high degree of precision; a single series of say, eight circummeridian zenith distances of a star south of the zenith, combined with an equal number of a star at nearly the same distance to the north of the zenith, would be sufficient. If I were to have again under my direction a triangulation of Java or a similar mountainous country, I certainly should prefer this method to that which has been followed. Moreover every mountain offers a wide field of research; and very interesting results might be attained by executing a large number of measures of plumbline deviation and gravity in the whole region affected by a vulcano.

As YVON VILLARCEAU has shown, the deviations of the astronomical azimuths from the geodetical ones may be expressed in deviations of longitude: unfortunately they must then be multiplied by the cosecant of the latitude, a factor, having for the 20 stations, where azimuths were determined, a mean value of more than 8. Moreover the said differences were too much affected by the accumulation of errors in the horizontal measures; so the results of this reduction were untrustworthy. They gave, (and this is not to be wondered at) improbably large deviations in longitude.

Much smaller discrepancies were obtained by comparing with the triangulation the differences of longitude which I determined, in conjunction with the Assistants JAEGER and VOSWINKEL DORSELEN, by the telegraph, in the years 1859—1863, before the resumption of the suspended triangulation. Our stations were not identical with those of the triangulation, but the relative positions have since been determined and allowed for. Though the comparisons are only eight in number, they show clearly the attraction by land.

Utrecht, February 19, 1901.

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Chemistry. — Dr. ERNST COHEN and E. H. BÜCHNER: „*On* ETARD's *Law of Solubility.*" (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. In 1894 ETARD [1]) formulated the following rule: When the solubility of different salts at different temperatures is expressed in grams of the salt per 100 grams of the saturated solution, the curves representing the solubility as a function of the temperature are straight lines and may be represented by an equation of the form $y = a + bt$. ETARD has determined the solubility of a number of salts in water (and other solvents); in some cases the temperature was so high that it came near to the melting point of the dissolved salts.

2. ETARD's views have passed into the literature (books of reference) and thus we find in the second edition of the *Physikalisch-chemische Tabellen* of LANDOLT and BÖRNSTEIN the accompanying solubility equation ($y = a + bt$) for each of the salts investigated by ETARD.

3. Knowing the difficulty of preparing a really saturated solution of any salt, that it has been proved necessary to shake or stir the particular solvent for a long time (1—3 hours) with an excess of the finely powdered salt at a constant temperature, it is surprising to find ETARD making the following statement: „pour obtenir une solution saturée de sel dans l'eau, il suffit de mettre dans un verre de Bohême un mélange de sel *concassé* et d'eau à volumes sensiblement égaux .... le thermomètre destiné à prendre les températures sert en même temps d'agitateur ... La rapidité de la saturation est telle dans les conditions que je viens d'indiquer, qu'on peut, pendant l'ascension continue mais très lente du thermomètre agitateur, prendre autant d'échantillons qu'on le désire de la solution parfaitement saturée aux températures t^0, $t_1{}^0$, $t_2{}^0$, $t_3{}^0$ ..... La régularité et la concordance des résultats suffiraient à démontrer la vérité de l'affirmation précédente. Cependant des expériences comparatives ont encore été faites pour la mettre hors doute, et elles ont montré qu'en effectuant la saturation dans un ballon agité pendant des heures, ainsi qu'on le recommande souvent, on n'arrive pas à une précision plus grande. Cela sont des précautions illusoires".

4. Investigations conducted by one of us with Mr. KOHNSTAMM some years ago [2]) on the solubility of cadmium sulphate had shown

[1]) WIEDEMANNS Annalen, N. F. 65 (1898) 344.

[2]) Annales de chimie et de physique, 7e série t. II, août 1894; t III, Octobre 1894.

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that the solutions used by ETARD in this case were quite unsaturated and that his figures for some temperatures were about 35 pCt. below the truth. The new figures were confirmed by the simultaneously conducted experiments of the Physikalisch-Technische Reichsanstalt at Charlottenburg (MYLIUS and FUNK)[1]) as shown by the subjoined table:

	100 grams of water dissolve grams of $CdSO_4$.		
Temperature.	ETARD.	COHEN & KOHNSTAMM.	MYLIUS & FUNK.
0°	55.52	75.52	75.47
10°	60.92	75.90	76.00
15°	63.77	76.11	76.05.

Later investigations on the solubility of zinc sulphate by CALLENDAR and BARNES[2]) and COHEN[3]) as well as the elaborate determinations published by the Reichsanstalt as regards a number of other salts created a suspicion that also in those cases ETARD's determinations had not been made with saturated solutions. The above mentioned law of solubility stands or falls, of course, with the correctness of ETARD's measurements. We have, therefore, carefully tested that law in a number of cases where very trustworthy determinations of the solubility have been executed (this number is comparatively small) and the result is given in the following lines.

5. ANDREAE's determinations[4]) have been conducted with great care. He took great pains to keep temperatures constant and was only satisfied when he had obtained the same result by three different methods. His determinations are certainly the most reliable ones which have ever been made in this direction.

In the following table we give the results of ANDREAE for $NaCl$, KCl, K_2SO_4, KNO_3, recalculated by ETARD's method. Under ETARD are given the solubilities derived from his own determinations (or from his equations) whilst along with ANDREAE's figures the temperature coefficient of the solubility is given which according to ETARD, must be constant for each salt.

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[1]) B. B. 30 (1897) 824.

[2]) Proc. Royal Society, 62 (1893) 147.

[3]) Proceedings Kon. Akad. v. Wetenschappen 30 Dec. 1899. 334. Zeitschrift für physikalische Chemie 34. (1900) 179.

[4]) Journal für praktische Chemie, N. F. 29 (1884) 456.

	NaCl.			KCl.			K_2SO_4.			KNO_3.		
	ANDREAE.	$\frac{\Delta L.}{\Delta t.}$	ETARD. $y=25{,}8+0{,}0248\ t.$	ANDREAE.	$\frac{\Delta L.}{\Delta t.}$	ETARD. $y^{+25}_{-11}=19.6+0.1916\,\theta$ $y^{+242}_{+25}=26.5+0.10\,3\theta$	ANDREAE.	$\frac{\Delta L.}{\Delta t.}$	ETARD. [1] $y=7.5+0.107\ t.$	ANDREAE.	$\frac{\Delta L.}{\Delta t.}$	ETARD. $y^{70}_{20}=24+0.71\,\theta$
0°	26.27		25.8	21.87		21.70	6.85		7.5	11.72		—.—
		0 000			0.202			0,160			0.556	
4°	26,27		25.90	22.68		22.47	7.49		7.93	—.—		—.—
		0.906			0.186			0 160				
10°	26.305		26.05	23.80		23.62	8.44		8.57	17.28		—.—
		0.007			0.174			0.156			0.673	
20°	26.38		26.29	25.54		25.54	10.00		9.64	24.09		24.0
		0.011			0.161			0.148			0 744	
30°	26.49		26.54	27.15		27.01	11.48		10.71	31.45		31.1
		0.015			0.148			0.138			0.754	
40°	26.64		26.79	28.63		28.05	12.86		11.78	38.99		38.2
		0.019			0.137			0.130			0.710	
50°	26.83		27.04	30.00		29.09	14.16		12.85	46.01		45.3
		0.021			0.126			0.122			0.626	
60°	27.04		27.28	31.26		30.13	15.38		13.92	52.35		52.4
		0.024										
70°	27.28		27.53	—.—		—.—	—.—		—.—	—.—		—.—
		0.026										
80°	27.54		27.78	—.—		—.—	—.—		—.—	—.—		—.—

1) C. R. 106 (1888) 208.

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It will be seen that in ANDREAE's determinations there is no question of a rectilinear course of the solubility line. The temperature coefficient constantly changes.

6. If to this we add the table of solubility for zinc sulphate as obtained from the concordant determinations of CALLENDAR and BARNES and COHEN

TEMPERATURE.	SOLUBILITY.	$\frac{\Delta L.}{\Delta t.}$
— 5°.0	28.21	
		0.260
0°.1	29.54	
		0.274
9°.1	32.01	
		0.290
15°.0	33.72	
		0.288
25°.0	36.60	
		0.328
30°.0	38.24	
		0.346
35°.0	39.97	
		0 305
39°.0	41.19	

it may also be observed that contrary to ETARD's data, the temperature coefficient is not constant. ETARD seems to have worked here again with unsaturated solutions.

He found the solubility 29.1 at + 1°
and 40.9 at + 49°

ETARD's curve shows nothing of the existence of a transition at 38°.5 which has been proved to exist by a number of methods.

7. The following table relates to cadmium sulphate:

	SOLUBILITY.		
TEMPERATURE.	ETARD.	MYLIUS en FUNK. COHEN en KOHNSTAMM.	
0°	35 7		43.01
10°	37.5		43.18
30°	42.0		43.75
86°	43.5	85°	39.6
94°	41.6	95°	38.1

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As will be seen, ETARD has experimented here below 86° with unsaturated and above 86° with supersaturated solutions.

8. Finally, it is shown from the latest determinations which have been executed with great care and accuracy in the Physikalisch-Technische Reichsanstalt by DIETZ, FUNK, v. WROCHEM and MYLIUS [1]), that ETARD when he determined the solubility of the salts investigated by these authors has always worked with unsaturated solutions. In some cases the existing differences are not large. It is not worth while to insert here all the tables as the general result seems to be thoroughly established.

9. LENOBLE [2]) pointed out in 1896 that the data formerly communicated by ETARD did not lead to straight lines but to curves of the fourth degree or higher with slight curvature. As it now appears that ETARD's original material does not represent the true state of affairs, a closer investigation in this direction has become superfluous.

Result of the Investigation.

ETARD's law of solubility is not in agreement with the facts; a simple relation like this between the solubility of salts and the temperature does not seem to exist. Repetition of ETARD's experiments at high temperatures is desirable.

Amsterdam, Chem. Lab. University, February 1900.

Mathematics. — Prof. J. C. KLUYVER: "*On the expansion of a function in a series of polynomials.*"

According to BOREL's remark [3]) the fundamental problem consists in expanding $1 : 1-x$. For, having once obtained an expansion of the form

$$\frac{1}{1-x} = 1 + \sum_1^\infty T_n(x) = 1 + \sum_1^\infty \left(a_{1n}\, x + a_{2n}\, x^2 + a_{3n}\, x^3 + \ldots a_{nn}\, x^n \right)$$

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1) Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt. Bd. III, 427.

2) Bulletin de la Société Chimique de Paris, XV (1896) 54.

3) Annales de l'école normale, t. 16, p. 132.

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that can be rendered converging in every finite region of the x-plane, not enclosing any part of the straight line $(+1, +\infty)$, from

$$f(x) = \sum_0^\infty c_m (x-a)^m$$

we may deduce

$$f(x) = c_0 + \sum_1^\infty U_n(x-a) = c_0 + \sum_1^\infty \left[\alpha_{1n} c_1 (x-a) + \alpha_{2n} c_2 (x-a)^2 + \ldots \alpha_{nn} c_n (x-a)^n \right],$$

and the series of polynomials $U_n(x-a)$ can be made to represent $f(x)$ in every finite region of MITTAG-LEFFLER's "star".

Solutions of the fundamental problem are given by MITTAG-LEFFLER [1]), PAINLEVÉ [2]) and others; still as yet new solutions are not devoid of interest. Perhaps the solution described here is not behind in point of simplicity at least from a theoretical point of view.

As was shewn by PAINLEVÉ the problem of expanding $1 : 1-x$ is connected with a problem of conformal representation implying a certain want of determinateness. This problem requires the mapping of the interior of a u-circle, centre the origin and radius unity, on the interior of a nodeless closed z-curve, going round the origin and passing through $z=+1$. The homologues of $u=0$, $u=+1$ are to be the points $z=0$, $z=+1$; moreover the shape of the z-curve must be made to depend on a single or on several arbitrary parameters in such a manner, that by their assuming appropriate values the z-curve takes more or less elongated forms, varying from a z-circle, centre the origin, to an area of infinitesimal breadth covering the stroke $(0, +1)$.

In no other way is the choice of the z-curve limited. We take it here to be an ellipse having one focus in $z=0$ and the farther extremity of the axis major in $z=+1$.

SCHWARZ's functional relation

$$z = c \sin\left\{ \frac{\pi}{2K} sn^{-1} \frac{u}{\sqrt{k}} \right\}$$

makes a u-circle and a z-ellipse conformal areas; since however by this formula the centres of both curves are corresponding points, and in our case the centre of the circle should be the homologue of one of the foci of the ellipse, a slight alteration is necessary.

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[1]) Acta Mathematica, t. 23, p. 43 and t. 24, p. 183 and 205.

[2]) Comptes rendus, 23 May and 3 July 1899.

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It will be seen that the correspondence defined by the equation

$$z = \frac{4q^{1/2}}{(1+q^{1/2})^2} \sin^2 \left\{ \frac{\pi}{2K} \, sn^{-1} \sqrt{\frac{u}{k}} \right\},$$

meets all requirements.

As to k, K and q, they are the usual JACOBIAN constants in the theory of elliptic functions; we will consider k and K as functions of q, thus making the latter quantity serve as an arbitrary real parameter able to assume all values between 0 and 1. Putting

$$\varepsilon = \frac{2q^{1/2}}{1+q},$$

the functional relation between u and z maps the u-circle on a z-ellipse represented in polar coordinates by the equation

$$R = \frac{1-\varepsilon}{1-\varepsilon \cos \varphi}.$$

When q tends to zero, the excentricity ε vanishes, the z-ellipse becomes a z-circle and ultimately we have $z = u$: on the contrary when q approaches its upper limit unity, the z-ellipse transforms itself into a narrow loop stretched round the stroke $(0, +1)$.

Obviously we may deduce from the functional relation an expansion of z in ascending powers of u. Writing

$$z = \frac{2q^{1/2}}{(1+q^{1/2})^2} \sum_1^\infty C_h u^h$$

the coefficients C_h are obtainable by means of the differential equation

$$u(k-u)(1-ku)\frac{d^2z}{du^2} + \frac{1}{2}[k-2u(1+k^2)+3ku^2]\frac{dz}{du} - \frac{\pi}{4K^2} z = \\ = \frac{2q^{1/2})}{(1+q^{1/2})^2} \cdot \frac{\pi}{4K^2}.$$

We shall find for the first and second terms [1])

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[1]) The notation of the ϑ-constants is that of TANNERY and MOLK, Éléments de la théorie des fonctions elliptiques.

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$$C_1 = \frac{2}{\vartheta_2^2\,\vartheta_3^2}, \quad C_2 = \frac{2\,(\vartheta_2^4 + \vartheta_3^4 - 1)}{3\,\vartheta_2^4\,\vartheta_3^4}$$

and we may then use the relation

$$C_{h+1} = \frac{4\,[h^2\,(\vartheta_2^4 + \vartheta_3^4) - 1]}{(2h+1)(2h+2)\,\vartheta_2^2\,\vartheta_3^2}\,C_h - \frac{(h-1)(2h-1)}{(h+1)(2h+1)}\,C_{h-1}$$

to obtain the higher coefficients.

Similarly it is possible to expand z^n. For z^n as well as z itself is simply an aggregate of cosines of constant multiples of the quantity

$$\beta = \frac{\pi}{2K}\,sn^{-1}\sqrt{\frac{u}{k}},$$

and the expansion of $\cos 2m\beta$ gives no more trouble than that of $\cos 2\beta$. In particular it should be noticed that the series for z^n begins with the term u^n.

The foregoing considerations enable us to express the function $1 : 1 - xz$ as an integral series of u. For, in fact, we have only to expand the different powers of z in the series

$$1 + xz + x^2z^2 + x^3z^3 + \ldots.$$

and to arrange the result according to ascending powers of u.

In this way we obtain an expansion of the form

$$\frac{1}{1-xz} = 1 + \sum_1^\infty T_n(x, q)\,u^n,$$

where the coefficient $T_n(x, q)$ is a polynomial in x of order n, the coefficients of the polynomial involving the parameter q.

Putting now $x = \varrho e^{i\vartheta}$ we will ask under what conditions as to x and to q this u-series has its radius of convergence at least equal to unity. This point is examined in the following way. Suppose u to move at random through the interior of the u-circle, centre the origin and radius unity, then z simultaneously moves within the corresponding z-ellipse and the motion of the point xz is restricted to take place in the interior of a second ellipse of the z-plane. Evidently this xz-ellipse is obtained by turning the z-ellipse round $z = 0$ through an angle θ, stretching at the same time its radii vectores in the ratio $\varrho : 1$. Hence if only the point $z = 1$ lies outside this xz-ellipse, given by the equation

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$$R = \frac{(1-\varepsilon)\,\varrho}{1-\varepsilon\cos(\phi-\theta)},$$

the function $1 : 1 - xz$ remains uniform and finite, whatever may be the position of u within the u-circle or even on its boundary. Therefore as soon as x and q be such that

$$1 > \frac{(1-\varepsilon)\,\varrho}{1-\varepsilon\cos\theta},$$

or what is the same that

$$\varrho < \frac{1}{1-\varepsilon} - \frac{\varepsilon}{1-\varepsilon}\cos\theta,$$

the u-series will converge unconditionally for $|u| \leqq 1$.

We assume x and q to satisfy the condition imposed upon them and put $u = +1$; thus we obtain

$$\frac{1}{1-x} = 1 + \sum_{1}^{\infty} T_n(x, q),$$

a development of $1 : 1-x$ holding good for all points x inside the limaçon

$$\varrho = \frac{1}{1-\varepsilon} - \frac{\varepsilon}{1-\varepsilon}\cos\theta.$$

This limaçon has its acnodal point in $x = 0$ and the nearer vertex in $x = 1$. Its shape depends on the value of q; by variating this parameter we may regulate to a certain extent the region of convergence of the series of polynomials. Take $q = 0$ and the limaçon degenerates into a circle, centre $x = 0$, radius unity. Suppose q tending to its upper limit and the limaçon covers larger and larger parts of the x-plane. Ultimately for $q = 1$ the limaçon would enclose all points x of the plane except those lying on the straight line $(+1, +\infty)$.

Thus we infer that the expansion of $1 : 1-x$ can be made to converge in every finite region of the plane not including a part of the line $(+1, +\infty)$ and we may use it in the manner indicated at the beginning to form an expansion representing a given function $f(x)$.

So, for instance, taking $q = e^{-\pi}$, we have for all points x inside the limaçon

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$$\varrho = 1.663 - 0.663 \cos \theta,$$

$$\frac{1}{1-x} = 1 + [0.5785\, x] + [0.2133\, x + 0.3347\, x^2] +$$
$$+ [0.0968\, x + 0.2468\, x^2 + 0.1936\, x^3] +$$
$$+ [0.0488\, x + 0.1575\, x^2 + 0.2142\, x^3 + 0.1120\, x^4] +$$
$$+ [0.0262\, x + 0.0978\, x^2 + 0.1762\, x^3 + 0.1652\, x^4 + 0.0648\, x^5] +$$
$$. . . . . .$$

If we now multiply the coefficients of $x^0, x^1, \ldots x^5, \ldots$ respectively by $0, 1, 0, -\frac{1}{3}, 0, \frac{1}{5}, \ldots$, that is by the corresponding coefficients of the power series

$$lg\ tg\ x = \frac{x}{1} - \frac{x^3}{3} + \frac{x^5}{5} \ldots,$$

we obtain the expansion

$$lg\ tg\ x = [0.5785\, x] + [0.2133\, x] + [0.0968\, x - 0.0645\, x^3] +$$
$$+ [0.0488\, x - 0.0714\, x^3] + [0.0262\, x - 0.0587\, x^3 + 0.0130\, x^5] + \ldots,$$

and the equivalence of the function and the series is valid for all points common to the interiors of the limaçons

$$\varrho = 1.663 \pm 0.663 \sin \theta.$$

And again in the same way we deduce from

$$\frac{1}{\sqrt{1-x}} = 1 + \frac{1}{2}x + \frac{3}{8}x^2 + \frac{5}{16}x^3 + \frac{35}{128}x^4 + \frac{63}{256}x^5,$$

$$\frac{1}{\sqrt{1-x}} = 1 + [0.2892\, x] + [0.1066\, x + 0.1255\, x^2] +$$
$$+ [0.0484\, x + 0.0925\, x^2 + 0.0605\, x^3] +$$
$$+ [0.0244\, x + 0.0592\, x^2 + 0.0669\, x^3 + 0.0306\, x^4] +$$
$$+ [0.0131\, x + 0.0367\, x^2 + 0.0551\, x^3 + 0.0452\, x^4 + 0.0159\, x^5] + \ldots,$$

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the region of convergence being the same as for the expansion of $1:1-x$.

For a test we may make the substition $x=-1$; we shall find

$$\frac{1}{2} = 0.5000 = 1-0.5785+0.1214-0.0436+0.0065-0.0042+\ldots$$
$$= 0.5016+\ldots,$$

$$lg\,tg(-1) = -0.7854 = -0.5785 - 0.2133 - 0.0323 +$$
$$+ 0.0266 + 0.0195 + \ldots = -0.7820 + \ldots,$$

$$\frac{1}{\sqrt{2}} = 0.7070 = 1 - 0.2892 + 0.0189 - 0.0164 - 0.0015 -$$
$$- 0.0022 + \ldots = 0.7096 + \ldots.$$

Phycics. — Prof. J. D. VAN DER WAALS on: "*The equation of state and the theory of cyclic motion.*" II. (Continued from page 528).

Before we are able to calculate the equation for the equilibrium and the entropy and the specific heat of a substance with triatomic molecules, we must first know the mode of motion. If the motion should be such, that the first atom is placed exactly in the centre of gravity, and consequently only the two other atoms move, such a molecule must be regarded as a diatomic one, and the equation of the equilibrium will be again equal to:

$$\left(p+\frac{dP_v}{dv}+\frac{dP_b}{db}\right)(b-b_0) = RT.$$

But the value represented by b_0 will include besides the space of the moving atoms, also the space occupied by the stationary atom.

If the motion of the three atoms relative to their centre of gravity should be such that the distance of one of them quite determines the place of the two others, as would be the case when they move along three lines, which enclose constant angles, and if the case is therefore to be considered as a vibrating system with one degree of freedom, then such a molecule must be treated in our considerations as a diatomic one.

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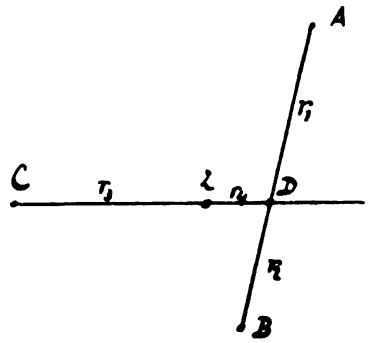

Only if the motion of two of the three atoms relative to each other is such, that it is independent of the motion of the third atom relative to the centre of gravity of the two first-mentioned, the molecule may be called a triatomic molecule also from our point of view, and we shall find a greater specific heat and a modified equation of state.

Let Z in the figure be the centre of gravity of the molecule, and A, B and C indicate the instantaneous position of the three atoms. If D is the centre of gravity of A and B, then the points C, Z and D must of course lie on the same straight line. Let us take the distances $DA = r_1$, $DB = r_2$, $CZ = r_3$ and $DZ = r_4$. Let us now imagine the motion of the atoms to be such that A and B move along their connecting line, and that at the same time, but independent of this, C and D approach each other. Then the vis viva of the first motion may be represented by:

$$B_1 (r_1 - r_{01})^2 \dot{s}_1^2 + B_2 (r_2 - r_{02})^2 \dot{s}_2^2$$

and that of the second motion by:

$$C_3 (r_3 - r_{03})^2 \dot{s}_3^2 + C_4 (r_4 - r_{04})^2 \dot{s}_4^2.$$

Then $A (v-b)^{2/3} \dot{s}^2$ added to the sum of these quantities represents the whole vis viva.

From this we deduce for the equation of the equilibrium:

$$\frac{dL}{db} + p + \frac{dP_v}{dv} = 2\left\{\frac{L_1}{r_1 - r_{01}}\frac{dr_1}{db} + \frac{L_2}{r_2 - r_{02}}\frac{dr_2}{db} + \frac{L_3}{r_3 - r_{03}}\frac{dr_3}{db} + \frac{L_4}{r_4 - r_{04}}\frac{dr_4}{db}\right\}$$

Let us call the increase of volume in consequence of the existence of the first motion:

$$b_1 - b_{01} = S_1 (r_1 - r_{01}) + S_2 (r_2 - r_{02})$$

and in consequence of the existence of the second motion:

$$b_2 - b_{02} = S_3 (r_3 - r_{03}) + S_4 (r_4 - r_{04}).$$

The way in which in these expressions r_1 and r_2 depend on each

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other, is known, just as that of r_3 and r_4; r_1 and r_3 however must be considered to be independent of each other at any moment. The sum of $b_1 - b_{01}$ and $b_2 - b_{02}$ is the quantity which we may consider as the increase of volume of the molecule, and so:

$$b - b_{01} = (b_1 - b_{01}) + (b_2 - b_{02}).$$

On account of the independence of the two atomic motions, we get therefore two equations of the equilibrium:

$$\frac{dL}{db_1} + p + \frac{dP_v}{dv} = \frac{2(L_1 + L_2)}{b_1 - b_{01}}$$

and

$$\frac{dL}{db_2} + p + \frac{dP_v}{dv} = \frac{2(L_3 + L_4)}{b_2 - b_{02}}$$

the former applying to the direction in the molecule which connects A and B, the latter for the direction which connects C and D. In other words, the molecule has two directions, according to which it can possess a different degree of compressibility. A form for the potential energy, which does not take these different properties in different directions into account, is therefore insufficient. The thermodynamic deduction of the equation of the equilibrium is therefore wrongly simplified by assuming the quantity P_b, and we should act more in accordance with the difference in properties in the two directions by introducing two quantities P_{b1} and P_{b2}. By means of them we may write then:

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b1}}{db_1}\right)(b_1 - b_{01}) = 2(L_1 + L_2) = RT$$

and

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b2}}{db_2}\right)(b_2 - b_{02}) = 2(L_3 + L_4) = RT.$$

If we calculate in the same way as is done for diatomic molecules on page 523, the value of dQ, we find for triatomic molecules, the atoms of which move in the way described:

$$dQ = L_0\, d\,log\,[(v-b)^{2/3} L_0] + (L_1 + L_2)\, d\,log\,[(b_1 - b_{01})^2 (L_1 + L_2)] +$$

$$+ (L_3 + L_4)\, d\,log\,[(b_2 - b_{02})^2 L_3 + L_4)].$$

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If we put $\frac{L_1 + L_2}{L_0} = \frac{1}{3} = \frac{L_3 + L_4}{L_0}$, we get:

$$\eta = R\{log\,(v-b)\,T^{3/2} + log\,(b_1-b_{01})\,T^{1/2} + log\,(b_2-b_{02})\,T^{1/2}\}$$

and therefore for the value of the specific heat at $v = \infty$:

$$C_v = R\left\{3/2 + 1/2 + 1/2 + \frac{Td\,(b_1-b_{01})}{(b_1-b_{01})\,dT} + \frac{Td\,(b_2-b_{02})}{(b_2-b_{02})\,dT}\right\}.$$

If we take for P_{b1} the form: $P_{b1} = \frac{1}{2}\,\alpha_1\,(b_1-b_{01})^2$ and in the same way for P_{b2} the form: $P_{b2} = \frac{1}{2}\,\alpha_2\,(b_2-b_{02})^2$, we find, supposing α_1 and α_2 independent of the temperature, from the equations of the equilibrium for which $v = \infty$, so from

$$\alpha_1\,(b_1-b_{01})^2 = RT$$

and

$$\alpha_2\,(b_2-b_{02})^2 = RT$$

both $\frac{Td\,(b_1-b_{01})}{(b_1-b_{01})\,dT}$ and $\frac{Td\,(b_2-b_{02})}{(b_2-b_{02})\,dT}$ equal to $\frac{1}{2}$, and we get:

$$C_v = \frac{7}{2}R \text{ and } C_p = \frac{9}{2}R,$$

and consequently

$$\frac{C_p}{C_v} = 1 + \frac{2}{7} = 1{,}2857.$$

For carbonic acid values for this relation are given varying from 1,274 to 1,322 [1]). For N_2O the values vary from 1,267 to 1,327. For SO_2 we find the values from 1,238 to 1,262.

In this calculation of the specific heat both of diatomic and of triatomic molecules, we have taken P_b as independent of the temperature, and on the supposition that $P_b = \frac{1}{2}\,\alpha\,(b - b_0)^2$, we have found a contribution to C_v of the same amount, as if there were in each case one degree of freedom more for the atomic motion than we assumed. If we had taken α as depending on the temperature, we should have found another amount for this contribution to C, which we may regard as a kind of potential energy. Specially if we

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1) See O. E. MEYER: Die kinetische Theorie der Gase. 1877 pag. 91.

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put α as proportional to the temperature, this contribution to C_v is equal to zero, as is evident without further calculation, if we put for the equation of the equilibrium at $v = \infty$:

$$\alpha' T (b - b_0)^2 = RT.$$

If we want to make the calculated value of C_v agree with the above mentioned, we have to assume every time one degree of freedom more for the atomic motion, than we put above. For the diatomic molecules we have then to assume besides the radial motion a motion normal to the radius vector. For the triatomic molecules we have then to assume besides the motions already assumed, still other motions, e.g. such a one that the line which connects A and B, leaves the plane of the figure, and that the line which connects C and D rotates in the plane of the figure.

Accordingly on the supposition that α is proportional to T, we find the potential energy of the molecule (i. e. the amount with which the total energy exceeds the vis viva) equal to zero, as appears from:

$$\varepsilon = F(T) + P_v - T\left(\frac{dP_v}{dT}\right)_v + P_b - T\left(\frac{dP_b}{dT}\right)_b.$$

For then $T\left(\frac{dP_b}{dT}\right)_b$ is always equal to P_b.

But it was not chiefly the calculation of the specific heat of the complex molecules, which induced me to this investigation. And though I am of opinion that its true knowledge is urgently required for getting an insight into the way in which atoms are grouped in the molecule and move relatively to each other, and though I think that through its value we shall often be able to take a decision, when other methods for the determination of the formula for the structure of the molecule fail, there is as yet still too little experimental material at hand to test different ideas which might suggest themselves. The prevailing opinion, that $\frac{C_p}{C_v}$ must decrease with the number of atoms, may be true in general, still there are remarkable exceptions. So the value of $\frac{C_p}{C_v}$ for NH_3 found experimentally is not in accordance with what we should expect for a tetratomic molecule. It points more to a molecule in which not four, but only three atoms move with respect to the centre of

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gravity. This leads to the idea that the atom N is placed in the centre of gravity of the three atoms H and does not take part in the atomic motion.

But let us now return to what I consider as the principal part of this investigation, viz. the two equations of equilibrium:

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b1}}{db_1}\right)(b_1 - b_{01}) = RT$$

and

$$\left(p + \frac{dP_v}{dv} + \frac{dP_{b2}}{db_2}\right)(b_2 - b_{02}) = RT.$$

There are two cases in which we might substitute one single equation of state for these two equations.

1st if $\frac{dP_{b1}}{db_1}$ could be taken as very great with respect to $\frac{dP_{b2}}{db_2}$, or rather if we assume $P_{b1} = \frac{1}{2}\alpha_1 (b_1 - b_{01})^2$ and $P_{b2} = \frac{1}{2}\alpha_2 (b_2 - b_{02})^2$ α_1 as being very great with respect to α_2. In this case $b_1 - b_{01}$ is small with respect to $b_2 - b_{02}$ and $b_2 - b_{02}$ may be equated to $b - b_0$. The equation of state becomes then:

$$\left\{p + \frac{dP_v}{dv} + \alpha_2 (b - b_0)\right\}(b - b_0) = RT,$$

just as for a diatomic molecule.

2nd if $\alpha_1 = \alpha_2$. Then is $b_1 - b_{01} = b_2 - b_{02} = \frac{1}{2}(b - b_0)$, and we get:

$$\left\{p + \frac{dP_v}{dv} + \frac{\alpha_2}{2}(b - b_0)\right\}(b - b_0) = 2RT.$$

For the suppositions as to the value of α_1 and α_2 which lie between these two limiting cases, there remain two separate equations, but as an approximation it may be admissible to put in all cases:

$$\left\{p + \frac{dP_v}{dv} + \alpha (b - b_0)\right\}(b - b_0) = f\,RT,$$

if f has a value between 1 and 2.

For carbonic acid I had expected f to be little different from 2 — and with this value for f I have tested this equation of state of b to the series of values for this quantity which occur in the Chapter

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"Experiments of ANDREWS" in the first part of Continuity etc., in order to see whether the observed variability of b might be explained in this way. For the calculation of this series of values for b I had assumed, that $\frac{dP_v}{dv}$ is equal to $\frac{a}{v^2}$, for a I had put the value of 0.00874. It has afterwards been doubted whether the molecular pressure is expressed perfectly accurately by this simple value. Nevertheless this form has always seemed the only rational one to me, and the accuracy, with which by means of this form the coefficient of compressibility can be calculated, as I have shown in the paper, which has been inserted in the volume of the Archives Néerlandaises dedicated to Prof. LORENTZ [1]), has confirmed this opinion.

It is not to be expected that I should have hit upon the exact value of a, and in fact there is reason to assume, that a must be about 3 percent lower, as will be shown presently. From this follows that the series of values for b is not perfectly accurate either.

But as $\Delta b = \frac{\Delta a}{RT} \frac{(v-b)^2}{v^2}$, the error in b, which at $v = \infty$ equal to $\frac{\Delta a}{RT}$, will continually become smaller with decreasing volume, and become zero for the limiting volume; and as the value of b, as will appear presently, also decreases from a certain limiting value at $v = \infty$ to zero, it will have decreased approximately in the same proportion. Consequently the series of the given value may serve as a test for the given equation. The constants occurring in the equation will, however, get a value somewhat different from what they would have if they were derived from a perfectly correct series of values for b.

It is obvious that whatever formula we may take for the molecular pressure, we shall find a certain course in the value b, of such a nature that if we on the other hand presume this series of values of b, we can trace back every particular of the course of the pressure curve. It is only the question whether the course of the values found for b is such as we have a priori cause to expect. Now the series of values of b first fulfils the condition that for large volumes b does not sensibly differ and seems constant. Not before we get volumes of the order of b (formerly I had thought volumes of $2b$),

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1) Dr. G. BAKKER informs me, that he made such a calculation of the coëfficiënt of compressibility already 14 years ago. It appeared from some pages of a M.S. sent to me that he had calculated β for ether at 25° as equal to 0,000179.

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does this value decrease sensibly. And it seemed then to me a strong proof of the accuracy of the values chosen for the molecular pressure, that this condition was fulfilled in the values found for b. The proof becomes much stronger if we can show that the values found for b quite answer to a before calculated formula for this value. The endeavours for finding such a formula for b, made by BOLTZMANN, JÄGER, VAN LAAR, myself and several other investigators, have as yet always been based on the supposition, that the molecules are rigid bodies of a spherical shape. The endeavours have failed. Not only do they require hopelessly elaborate calculations, but I have had to convince myself that the calculated values of the coefficients found for such an equation cannot be in accordance with the observations. Now that I have found that for complex molecules of whatever shape, we find the same form for the equation of state of the substance as for a substance composed of simple molecules, I have thought that I might give up the rigidity and the spherical form of the molecules, and I have wished to try whether the compressibility of the molecules might be able to explain the decrease of b with the decrease of the volume. In the following pages I shall communicate the result, obtained in that investigation. Whether we have quite to reject the correctness of the considerations, on which the earlier attemps at the calculation of the variability of b are based, I shall not make bold to decide. I have only tried whether the equation:

$$\left\{p + \frac{a}{v^2} + \alpha(b-b_0)\right\}(b-b_0) = f\,RT$$

represents the value of b found at every value of v.

This formula gives a value of b which changes exceedingly little, if the value of v is great, and which decreases strongly for small values of v.

Let us begin with modifying the equation somewhat. Let us viz. introduce the limiting value of b for $v = \infty$. Let us represent it by b_g. It is calculated from:

$$\alpha(b_g - b_0)^2 = f\,RT.$$

If we write for $p + \frac{a}{v^2}$ its value viz. $\frac{RT}{v-b}$, we get:

$$\frac{b-b_0}{v-b} = f\left\{1 - \left(\frac{b-b_0}{b_g-b_0}\right)^2\right\}.$$

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Let us take the series of values of v and b for $t = 35°.5$ and for $t = 32°.5$, which temperatures differ so little that the same values may be assigned to the constants, and let us put $b_g = 0.0026$. Then two more constants occur in the equation, viz. f and b_0. For both we have some indication as to their value. For f we might take 2, and for b_0 (the smallest possible value which b can assume) I had thought that I might conclude to a value of $\frac{1}{4} b_g$ according to the earlier view of the cause of the variability. As f is much easier to calculate than b_0, which can only be found by solving an equation of the third degree, I took for b_0 the value 0.00065. For the value of f we find then, beginning with the smallest volume:

$$f = 2.114, \quad f = 2.08, \quad f = 2.175, \quad f = 2.14 \text{ etc.}$$

Then I increased b_0 a little, viz. so much that it became $0.0007 = \frac{1}{3,7} b_g$, and then we find with $f = 2$:

	calculated	found
$b = 0{,}001798$	$v = 0{,}002622$	0,002629
$b = 0{,}00184$	$v = 0{,}002731$	0,00275
$b = 0{,}00195$	$v = 0{,}003050$	0,003026
$b = 0{,}0020$	$v = 0{,}003213$	0,00321

For the great values of v, b draws so near to the limiting values, that here the list of values of b, which increase and decrease irregularly, are of no importance.

Only the value of v which is given for $b = 0{,}00234$ does not agree, but it would perfectly agree if we might put $b = 0{,}002295$.

As I observed above, if the course of the value of b is represented perfectly correctly by the equation, the isothermal calculated by the aid of it will have to possess all the peculiarities of the isothermal determined experimentally. So the value of v, for which $\frac{dp}{dv}$ and $\frac{d^2p}{dv^2}$ are equal to zero, will have to coincide with the critical volume and in the same way the value of $\frac{p_k v_k}{RT_k}$ will have to possess for that volume the value which the experiment has determined for it.

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Now if b is kept constant, the equation of state has shown such large differences between the calculated and the experimental values of v_k and $\frac{p_k v_k}{RT_k}$, that it is advisable to examine whether the variability of b according to the given formula can annihilate these differences.

For the determination of the critical point we have now the following equations:

$$p + \frac{a}{v^2} = \frac{RT}{v-b} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\frac{2a}{v^3} = \frac{RT}{(v-b)^2}\left(1 - \frac{db}{dv}\right) \quad \ldots\ldots \quad (2)$$

$$\frac{3}{v} = \frac{2\left(1 - \frac{db}{dv}\right)}{v-b} + \frac{\frac{d^2b}{dv^2}}{1 - \frac{db}{dv}} \quad \ldots \quad (3)$$

The last of these equations, in which neither p nor T occurs, will have to serve as a determination of v_k, and that in connection with:

$$\frac{b-b_0}{v-b} = 2\left\{1 - \left(\frac{b-b_0}{b_g-b_0}\right)^2\right\} \quad \ldots\ldots \quad (4)$$

Let us write (3) in the form:

$$\frac{3\,(v-b)}{2\,v} = 1 - \frac{db}{dv} + \frac{v-b}{2}\,\frac{\frac{d^2b}{dv^2}}{1 - \frac{db}{dv}} \quad \ldots\ldots \quad (5)$$

For the determination of the critical volume we have therefore to choose such a value for v, that the values for b, $\frac{db}{dv}$ and $\frac{d^2b}{dv^2}$, which according to (4) belong to it, satisfy (5).

From (4) we find:

$$\frac{db}{dv} = \frac{1}{1 + 2\left\{\left(\frac{v-b}{b-b_0}\right)^2 + \left(\frac{v-b}{b_g-b_0}\right)^2\right\}} \quad \ldots\ldots \quad (6)$$

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and

$$\frac{v-b}{2}\frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}=-\frac{db}{dv}\frac{2\left\{\left(\frac{v-b}{b-b_0}\right)^2+\left(\frac{v-b}{b_g-b_0}\right)^2-\left(\frac{v-b}{b-b_0}\right)^3\frac{\frac{db}{dv}}{1-\frac{db}{dv}}\right\}}{1+2\left\{\left(\frac{v-b}{b-b_0}\right)^2+\left(\frac{v-b}{b_g-b_0}\right)^2\right\}}. \quad (7)$$

Such a value for v satisfying (5) can only be found by repeated approximation. For this it is useful to get to know the course of b, $\frac{db}{dv}$ and $\frac{v-b}{2}\frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}$.

With regard to b we point out that at $v=\infty$ the value of b approaches b_g asymptotically, that b decreases continually with v and that v and b assume at the same time the value b_0.

So if we take two axes, a v axis and a b axis, and if we draw the point P_0, for which $v=b_0$ and $b=b_0$, then the line representing b, will ascend from the point P_0. The initial direction in P_0 is indicated by $\frac{db}{dv}=\frac{f}{1+f}$ or in our case by $\frac{db}{dv}=\frac{2}{3}$. The value of $\frac{db}{dv}$ is at $v=\infty$ equal to zero, but may become considerable if v is very small, and increase to $^2/_3$. This value of $\frac{d^2b}{dv^2}$ is always negative, but in the equation (5) this quantity does not occur separately; it occurs however, in the combination $\frac{v-b}{2}\frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}$. It appears from (7) that this expression is negative, and of the order of $\frac{db}{dv}$. The factor, with which $\frac{db}{dv}$ is to be multiplied in order to get this complex, is equal to 1, if $v=\infty$, and descends to zero with diminishing volume.

It was necessary that $\frac{db}{dv}$ is never greater than 1. For if $\frac{db}{dv}$ is larger than 1, $\frac{dp}{dv}$ is necessarily negative, and then we should get unstable

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phases for very small values of v, which is quite opposed to the experiment. With the coefficients found in the earlier attempts at explaining the variability of b, I repeatedly met such unstable phases.

It is obvious that a value for v, satisfying (5) can be found, and probably but a single value, if we pay attention to the fact that the first member varies regularly between the values $\frac{3}{2}$ and 0, and the second member between 1 and $^1/_3$.

But when determining the value of v which satisfies (5), we meet with the difficulty, that we must be able to calculate not only b, but also $\frac{db}{dv}$ and $\frac{d^2b}{dv^2}$ perfectly from the equations given for them, while a slight change in the value of f and b_0 might cause a very great change in the value of these quantities which is to be calculated. So the equation (5) is not perfectly satisfied, if we take v equal to the observed critical volume. With $b=216{,}7$ we calculate $v=0{,}004082$, and we find the value of $\frac{db}{dv}$ equal to 0,16 à 0,17 and for the relation $\frac{v-b}{2}\ \frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}$ and $\frac{db}{dv}$ the value 0.71. Now (5) may also be written:

$$\frac{3b}{1+2\left\{\frac{db}{dv}-\frac{v-b}{2}\ \frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}\right\}} \quad \ldots\ldots \quad (8)$$

and calculated with this we do not get back $v = 0{,}004082$, but $v = 0{,}00411$. With $b = 0{,}00223$, we find $v = 0{,}004406$, so the assumed critical volume, then $\frac{db}{dv} = 0{,}132$ and $-\frac{v-b}{2}\ \frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}$ has a value very near 0,1. Then we find from (8) $v = 0{,}000457$, so a greater difference between the two values calculated in different ways. But the cause of this may be that the given equation for the determination of b is drawn up to represent the series of values which I have calculated for them by aid of a not quite accurate value of a. And moreover it appears sufficiently from the

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deduction of the formula for b that it can only be meant as an approximation.

If we put in future for $\frac{db}{dv}$ as it is in the critical point α, and β for $-\frac{v-b}{2}\frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}$, then:

$$v_k = \frac{3b_k}{1+2(\alpha+\beta)}$$

$$RT_k = \frac{8}{27}\frac{a}{b_k}\frac{(1-\alpha-\beta)^2[1+2(\alpha+\beta)]}{1-\alpha}$$

$$p_k = \frac{1}{27}\frac{a}{b_k^2}\left[1+2(\alpha+\beta)\right]^2\left[4\frac{1-\alpha-\beta}{1-\alpha}-3\right]$$

If α and β are equal to 0, then we find the known values which have been calculated on the supposition of constant value of b.

Let us take $\alpha = 0{,}138$ and $\beta = 0{,}1$, which in the proximity of the critical point of carbonic acid is not exaggerated. From the series of values of b a value for $\frac{db}{dv} = \frac{1}{5}$ is even calculated, if v is between 0,00496 and 0,00321.

Then we find a very great difference in the critical volume, and the factor b_k descends even to 2,03 — to which must be added that b_k is smaller than b_g and may be put at about 0,86 b_g.

But RT_k and p_k are comparatively little influenced by this value of α and β. The factor with which $\frac{8}{27}\frac{a}{b_k}$ is to be multiplied, descends by it only from 1 to $1-\frac{1}{170}$. And the factor, with which $\frac{1}{27}\frac{a}{b_k^2}$ is to be multiplied in order to find p_k, rises from 1 to $\frac{7}{6}$. Therefore the value of $\frac{p_k v_k}{RT_k}$ will be smaller than is found on the supposition of constant b and that approximately in the same proportion, as is the case with v_k, which is in perfect accordance with the experiment.

For the value of $\left(\frac{pv}{RT}\right)_k$ we find the expression:

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$$\left(\frac{pv}{RT}\right)_k = \frac{3}{2}\,\frac{1}{1-\alpha-\beta} - \frac{9}{8}\,\frac{1-\alpha}{(1-\alpha-\beta)^2},$$

which leads to the wellknown value $^3/_8$, if α and β are 0 and descends to $\frac{1}{3,4}$ with the given value of α and β. From the determinations of VERSCHAFFELT we derive for this value $\frac{1}{3,56}$.

(To be continued.)

Physiology. — Dr. J. BRAND: "*Researches on the secretion and composition of bile in living men*". (Communicated by Prof. B. J. STOKVIS.)

Nine cases of cholecystotomy, performed in the surgical wards of the Binnen-Gasthuis at Amsterdam in the years 1896—1899, afforded the occasion, to examine in the first place the rapidity of the flow of human bile. The secretion is a continuous one, sinking during the night, and showing its minimum in the early hours of the morning. After awakening the flow is rising generally fastly and attains a maximum a few hours after midday. In the evening the flow of bile presents a second maximum, which is much smaller than the first. These maxima probably depend on the taking of meals. The quantity of bile produced in 24 hours may be as great as 1100 cc (so that it comes near the quantity of urine produced in the same time), the smallest quantity found was 500 cc. There was no difference in the concentration of the bile at different times of the day. The quantity of the produced bile is very little influenced by the body-weight; it is chiefly depending on metabolism, which is exactly measured by the quantity of the essential substances of the bile. The amount of solid matters in freely along the bile-ducts flowing human bile (bile of the liver) attains 1.41 pCt.; in bile, stored up in the gall-bladder, it can be as high as 20 pCt. The colour of human bile is a bright golden yellow one, and the amount of the colouring matter: the bilirubin is rather low: 0.06 pCt. Human bile contains besides bilirubine urobilinogen or properly speaking reduced urobiline in rather large quantities as a constant compound, and probably also very small quantities of haemato-porphyrine, which is almost never absent

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in bile of the gallbladder. As to the bile acids, the proportion between taurocholate and glycocholate in human bile was varying between 1.45 and 1.54. Conjugated or ether-sulphuric acids were also found in human bile, at the rate of 6.4 pCt.—11.7 pCt. of the sulphur they contained, to the sulphur of taurocholate.

The physico-chemical properties of human bile were examined with great care, as there are till now but very few investigations in that direction. The molecular concentration of human bile, with its neutral or alkaline reaction to litmuspaper, with a rather low viscosity (the amount of mucine in bile of the liver is varying between 0.2 and 0.9 percent), examined by the method of determining the lowering of the freezing point, proved to be almost perfectly equal to the molecular concentration of the blood. This fact, which was also stated for the bile of the gall-bladder, is a very remarkable one, in as much as the amount of water and solid matters in bile of the liver and in bile of the bladder can be most widely different; yet the molecular concentration remains invariably constant. It may therefore be concluded, that in the more concentrated bile, containing a large quantity of great molecules as bilious acids, bilirubine etc. the rate of inorganic salts and especially of Cl Na must be a low one. In fact in bile containing 3.7 percent of taurocholate the rate of inorganic salts proved to be 0.955 percent, in bile with 20.9 of taurocholate this rate being only 0.265 percent. During secretion of bile resorption of a salt-solution, which is isotonic with blood, must therefore undoubtedly take place in the bilious ducts and the gallbladder. Moreover the secretion of the mucous membrane of the bilious ducts and bladder being also isotonic with blood, there can be an exchange of molecules of salt for molecules of mucine, the molecular concentration i. e. the osmotic pression remaining unchanged. The influence of mucine in the process of resorption is not yet clearly determined. As a high amount of mucine accompanies as a rule a high amount of inorganic salts, it may be assumed, that mucine is influencing dissociation, or is linked to mineral compounds.

Finally, the electrolytic conducting power of bile was determined by KOHLRAUSCH's method. It proved to surpass the conducting power of blood, (λ 37° C = 18.21—18.30 + 10^{-7} in unities of mercury), as could easily be presumed by the great amount of salts it contained. Yet the rate of inorganic salts is no measure for electrolytic conductibility.

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Bacteriology. — Prof. M. W. BEIJERINCK presents a paper: "*On Oligonitrophilous Bacteria*".

By "Oligonitrophili" I understand those microbes, which develop in media to which are not purposely added nitrogen compounds, but without precautions having been taken to exclude the least traces of these compounds.

They give rise to two different series of „accumulation experiments", the development being caused: *First*, in the light, without any other source of carbon in the food but the carbonic acid of the atmosphere, when chromophyll-containing oligonitrophili are to be looked for. *Second*, in presence of a source of organic carbon in the medium, when colourless oligonitrophili may be expected. In both directions I have made many experiments, of which those in the light have a very slow course and are still in process; here follow some results concerning "accumulation experiments" with colourless oligonitrophili.

1. *Aërobiosis and Anaërobiosis in Oligonitrophili.*

The "elective culture" of oligonitrophili in nutrient liquids with organic carbon compounds, has first been practised by WINOGRADSKY, under circumstances which secured anaërobiosis [1]). He used 2 to 4 pCt. glucose solutions with the required mineral nutrients and 4 pCt. $CaCO^3$, but without purposely added nitrogen compounds. For the infection was used garden-soil, and he constantly obtained a culture of a microbe belonging to the butyric-acid ferments. The experiments were performed in ordinary glass jars under cotton-wool plugging, when first a rich culture of aërobics develops, which renders possible the life of the anaërobic oligonitrophilous butyric-acid ferment, called by WINOGRADSKY *Clostridium pasteurianum*. He also worked with pure cultures of this species at exclusion of air. When repeating his experiments I found that traces of nitrogen compounds are indispensable for success, and the same is the case for the aërobic oligonitrophili found by myself, so that in culture liquids, prepared with all the precautions that exclude the presence of compounds of nitrogen, as well with aërobiosis as with anaërobiosis in a nitrogen atmosphere, the growth of oligonitrophili is extremely feeble and soon ceases.

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[1]) Recherches sur l'Assimilation de l'Azote libre de l'Atmosphère par les Microbes. Archives des sciences biologiques. St. Pétersbourg. T. 3 N. 4. 1895. „Elective culture" is the name given by W. to the accumulation experiments.

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My own experiments differ from those of WINOGRADSKY by my having rendered possible either aërobiosis only, or by sufficiently promoting the access of oxygen at least partly to counteract the butyric-acid fermentation. So doing I came to the discovery of a not yet described genus of oligonitrophilous bacteria, belonging to the aërobics [1]). This genus, which is easily recognisable by the large dimensions of the bacteria, I will call *Azotobacter*. Hitherto I found two well distinguished species, one, *A. chroococcum*, is extremely common in garden-soil, the other, *A. agilis*, is as common in the canal-water of Delft.

Sufficient access of oxygen is easily to be obtained in my experiments by cultivating in thin liquid layers on the bottom of spacious ERLEMEIER-jars. As the butyric-acid ferment, however, can by no means do quite without oxygen, but, being „microaërophilous", does want oxygen, albeit of low tension for vigorous development (which has been overlooked by WINOGRADSKY), the regulation of the access of oxygen is not sufficient completely to keep this ferment out of the aërobic cultures. I have therefore tried to prevent its growth by selecting carbon sources which are well assimilated by *Azotobacter*, but cannot, or can only with difficulty give rise to butyric-acid fermentation. As particularly fit for this end I found to be: mannite in 2 to 10 pCt. solutions, and calcium propionate in $^1/_2$ pCt. solutions, of which the former is hardly, the latter not at all attacked by the butyric-acid ferment [2]). Less adapted for the experiments are cane-sugar and glucose, these sugars, especially the latter, easily getting into butyric-acid fermentation. But I must remark that a feeble butyric fermentation, at least when calcium carbonate is present, is by no means prejudicial to my experiment, as calcium butyrate, too, is a source of carbon easily assimilated by *Azotobacter*.

2. *Accumulation of Azotobacter chroococcum from Garden-soil.*

This species is obtained as follows.

In an ERLEMEIER-jar is introduced a thin layer of a not sterilised culture liquid of the following composition:

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1) More exactly of which one species is "macroaërophilous", the other "mesoaërophilous".

2) It is also possible to prevent butyric-acid fermentation by introducing a piece of pure red copper into the cultures, by which *Azotobacter* is not prejudiced. This artifice occurred to me by observing the flame reaction of copper, when burning in a BUNSEN-flame, common *Azotobacter*-films, grown without addition of copper, from a crude culture, in tap-water with 2 pCt. mannite and 0,02 pCt. $K^2H\,PO^4$, and infected with garden-soil.

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100 Gr. Tap-water [1]),
2 „ Mannite,
0.02 „ K^2HPO^4.

and for the infection is used a not too slight quantity, say 0.1 Gr. or more, of fresh garden-soil [2]).

Accordingly, other nitrogen compounds but the small quantities which occur in the tap-water and the infection material, are wanting. But by numerous experiments, made under very different circumstances, many of which with nutrient liquids prepared from pure destilled water, whose composition was thus perfectly known, I have, as said, come to the conclusion, that this slight quantity of compounds of nitrogen is absolutely necessary for the success of the experiments with *Azotobacter*, and that the same is true for WINOGRADSKY's *Clostridium pasteurianum.*

In presence of nitrogen compounds in a rather considerable quantity, e. g. 10 milligrams or more of potassium nitrate or ammonium phosphate per liter of culture fluid, *Azotobacter* is no more proof against the competition with the common nitrophilous microbes and does not develop. But this is by no means the case with *Clostridium pasteurianum*, which excellently develops even at much higher rates of nitrogen compounds, though only then when the nitrophilous microbes have nearly quite consumed those compounds, so that diphenylamin shows no more nitrates, NESSLER's reactive no more ammonia.

If the culture jars, prepared in the said way, are kept at 28° to 30° C. then, after 2 or 3 days, a floating film develops at the surface of the fluid, externally resembling *Mycoderma*, but consisting of *Azotobacter chroococcum*, and wherein, it is true, some other species of small bacteria are present but not in sufficient quantity to determine the character of the culture. These small bacteria have greater want of nitrogen than *Azotobacter*, but less than the common saprophytic "polynitrophilous" species; they may accordingly be called "mesonitrophilous". The best known instance of mesonitrophili is *Bacillus radicicola* of the tubercles on the roots of the Papilionaceae, but I have not succeeded to find this species in the crude *Azotobacter* accumulations. The mesonitrophili relate to *Azotobacter* as the vinegar bacteria to *Mycoderma* in the films which are found on flat beer, and their volume, when compared with that of *Azotobacter*

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[1]) The tap-water of Delft comes from the downs at Loosduinen.

[2]) From pasteurised soil aërobic oligonitrophili do not develop.

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itself, is so insignificant that at a chemical analysis of the culture, they would hardly be perceived. By carrying on the experiment with $^1/_2$ pCt. calciumpropionate as carbon source, instead of 2 pCt. mannite, and with garden-soil as infection material, after 3 or 4 days *Azotobacter*-films are obtained, in which microscopically no other bacteria at all are to be found but *A. chroococcum* only, and of which culture on solid media is necessary, in order to detect the not absolutely failing strange species.

Besides these small bacteria are sooner or later found in the *Azotobacter*-films a great number of Amoebae and Monads, sometimes also Infusoria. [1])

The common soprophytic bacteria, such as the fluorescents, the various species of *Aërobacter*, *Proteobacter*, *Saccharobacter*, and the hay bacteria, are quite wanting in the *Azotobacter*-films, although their germs abound in the infection material.

Moulds and yeast species, too, are in the beginning totally absent, so that the rough culture of *A. chroococcum* can be regarded as one instance more of a "perfect accumulation experiment", of which I recently described another case. [2])

The number of carbon compounds which can be assimilated by *A. chroococcum* is considerable. Thus mannite can be replaced by 2 to 10 pCt. cane-sugar, whereby, however, a more slimy film is formed, which sooner or later sinks down. For glucose, in quantities of 2 to 6 pCt., the same may be observed. But these two sugars, especially the latter, give most easily rise to butyric-acid fermentation, which, by the free acid, acts injuriously on the growth of *Azotobacter*. At simultaneous addition of calcicum carbonate a butyric-acid fermentation may first occur, which is succeeded, in the same culture, by the growth of an *Azotobacter*-film at the expense of the butyrate, and producing crystals of calcium carbonate. With galactose, levulose and maltose, I likewise obtained magnificent *Azotobacter* cultures; galactose gives with difficulty, levulose, on the other hand, gives easily rise to butyric-acid fermentation.

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[1]) Amoebae feed with great avidity on *Azotobacter* itself, and, multiplying very rapidly, can bring about much destruction in the cultures. They belong to different species, which also easily propagate on the solid medium, fit for the pure culture of *Azotobacter*. Thereon they produce the pure "veils of amoebae", free from bacteria, described by me at another occasion (Centralblatt für Bacteriologie Bd. 19, pag. 257, 1896 and Bd. 21, pag. 101, 1897) and hence, may be obtained in pure culture by the here described experiment, together with *Azotobacter*, and be cultivated with other microbes at will for nutriment. Brief, also for the study of Amoebae the *Azotobacter*-experiment forms the best starting point.

[2]) Centralblatt f. Bacteriologie, 2e Abt. Bd. 7, pag 35, 1901.

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With glycerin the experiments have a slower course; moreover only with solutions of 2 to 5 pCt. I could obtain closed *Azotobacter*-films, whilst 10 pCt. proved to be too concentrated. Milk-sugar is not assimilated by *Azotobacter*, but quite well by the butyric-acid ferment. Furthermore, the following substances are assimilated with variable intensity, the first best, the latter with more difficulty: propionates, butyrates, lactates, malates, succinates, acetates and citrates. Formiates and tartrates are not attacked at all.

As from this list we may safely conclude, that *Azotobacter* is able to assimilate still various other sources of carbon beside the here mentioned, the oxidising faculty of this bactery is evidently developed in a great many directions, and may perhaps be best compared to that of the fluorescents, which, however differ from *Azotobacter* by their much greater want of nitrogen, by which they belong to the polynitrophili.

The crude *Azotobacter*-film obtained in the way described, consists at first of extremely large short-rods of ca. 4 μ thick and 5 μ to 7 μ long, with rounded ends, and which often have the shape of diplococci. [1]) Mostly all are in rest but some specimens swim stately round. Remarkable is the presence of a lateral vacuole in some individuals.

The cell-wall is slimy and easily visible, or rendered visible by introducing some small bactery into the microscopic preparation, whereby the slimy coat, which in water alone is not to be seen, becomes distinct, as the small bacteria do not penetrate into it. At nutrition with mannite most individuals are filled with exceedingly small regularly placed drops of fat.

When the cultures grow older the floating film changes color and first becomes brown, later on sometimes even black. But this does not always occur and depends on known and unknown circumstances, Thus the color changes slowly or not at all at the direct nutrition with sugars, but the change can with certainty be expected when butyrates or propionates are used as carbon food, or, with sugars, in presence of calcium carbonate, and after previous butyric-acid fermentation.

The coloring matter is not soluble in the usual solvents as water, alcohol, chloroform, ether and CS^2, and is quite different from chromo-

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[1]) On propionates and acetates as sources of carbon, and with garden-soil for infection material, I have in these accumulation experiments sometimes obtained a much smaller form, which I consider as a variety of *A. chroococcum* and not as a separate species. A second variety of *A. chroococcum* I obtained from canal-water.

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phyll. It induced me to choose the word *chroococcum* for the name of the species.

With the change of color the microscopical appearance of the bacteria themselves changes also considerably. The dimensions grow smaller and the shape becomes more globulous, so that we should think to have common, even small micrococci before us, but at the partition these older cells remain united in sarcine lumps. The shapes of the involution forms of *Azotobacter* are very singular. They can attain gigantic dimensions, e. g. 10—15 μ, and remind of amoebes and yeast cells. They are especially met with in the *Azotobacter*-films of the crude cultures.

3. *Pure culture of Azotobacter chroococcum.*

The pure culture of this species from the crude floating film is easily effected by streaking it off on a culture plate of the following composition:

100	Gr.	Destilled water.
2	„	Agar.
2	„	Mannite.
0.02	„	$K^2 H PO^4$.

The 2 pCt. agar contain the other necessary mineral nutrients in sufficient quantity. Grown at 30° C. *Azotobacter* becomes after one day already visible as white, starch-like colonies, among the, for the greater part watery, transparent nitrophili. Though in the crude cultures the latter had slackened their growth, on the plates they again acquire a considerable development, evidently in consequence of the presence of nitrogen compounds in the agar. The number of the *Azotobacter*-colonies is always much smaller than might be expected from the number of germs brought on the plate, so that some attention is necessary to find them out when still young; but later they become quite distinct. On the said medium, if containing sufficient mannite, e. g. 5 to 10 pCt., the *Azotobacter*-colonies can grow a very long time, and thereby attain much greater dimensions than those of the nitrophili.

Contrary to what we have seen in the crude cultures, *Azotobacter* can develop in pure condition on the most different media. On broth gelatin it grows however slowly and little characteristically; it hardly or not liquefies the gelatin.

Grown in liquids the presence of small quantities of nitrogen compounds furthers considerably the growth of the pure cultures. Espe-

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cially nitrates are easily assimilated and may even be added to an amount of 0,1 pCt. Thus I sometimes, but not always, saw an enormous growth in

100	Gr.	Tap-water
2 to 10	„	Mannite
0.02	„	$K^2H\,PO^4$
0.1	„	$K\,NO^3$

With ammonia salts the growth of the pure cultures is slower than with nitrates, and the amounts which act not deleteriously, are slight. Still I saw a considerable development in

100	Gr.	Tap-water.
2 to 4	„	Glucose.
0.02	„	$K^2H\,PO^4$
0.02	„	$(NH^4)^2\,HPO^4$

Asparagin acts about as ammonia salts. Peptone is assimilated with great difficulty.

After being kept for some weeks the pure cultures, in particular with glucose as carbon food, grow dark brown, quite like the crude films mentioned above, and in other respects too, they seem somewhat to alter their character. I could at least in no way produce on nutrient liquids, with the pure cultures, the magnificent films which are obtained by the crude infections; the newly formed cells remaining constantly immersed. But I should call to mind that this is partly explained by the use of non-sterilised materials in the crude cultures, which of course cannot be used in the experiments with pure cultures.

The motility of this species is always restricted to a very small number of individuals. By this reason, as also in consequence of the slimy constitution of the cell-wall, the experiments to color the cilia had given no result in my laboratory. But Professor ZETTNOW at Berlin, whose advice I have asked, procured me very beautiful preparations, from which it is certain, that at least the great majority of the moving individuals, possess one polar cilium of nearly the same length as the body of the microbe itself.

4. *Azotobacter agilis.*

This species is obtained by the "accumulation experiment" described for *A. chroococcum*, with this difference, that the tap-water is

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replaced by canal-water [1]), and that the infection with soil is omitted, as the very question is to develop the oligonitrophili present in the canal-water itself. Good *agilis*-films are produced, when

100	Gr.	Canal-water.
2	„	Mannite
0.02	„	$K^2H\,PO^4$

in a thin layer is allowed to stand for some days at 30° C.

It is true that glucose is much better assimilated by *A. agilis* than mannite, but it causes more easily butyric-acid fermentation, which should here be avoided. Nevertheless I have in some cases obtained good results with glucose, and with cane-sugar also. Likewise when using $^1/_2$ pCt. calcium lactate, or $^1/_2$ pCt. calcium acetate. Even 2 pCt. alcohol is a very good source of carbon, but, like the last mentioned organic salts, produces an *agilis*-film much later than the different sugars. With propionates I obtained less good results, as therewith very numerous monads and amoebae originate, which feed on *agilis*.

The canal-water of Delft being rich in organic matter, the addition of a little $K^2\,HPO^4$ only is mostly also sufficient to form a beautiful film of *Azotobacter agilis*, which however, as a matter of course, remains poor in bacteria material.

The pure cultures are obtained in the same way as described for *A. chroococcum*. The best medium is

100	Gr.	Destilled or tap-water
2	„	Agar
2	„	Glucose
0.02	„	$K^2H\,PO^4$

In the streaks, inoculated on this medium the colonies of *agilis*, always intermixed with those of many other kinds of bacteria, among which *Azotobacter chroococcum* commonly occurs, are easily recognised after 24 hours already.

If in this latter solid medium the glucose is replaced by $^1/_2$ pCt. calcium propionate and if streaks are made of the crude culture, then also a considerable growth follows, and around the colonies of *A. agilis* a greenish diffusion zone arises, reminding of the coloring matter of the fluorescents.

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[1]) From the water of the North sea I could not obtain oligonitrophili.

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In the pure cultures of *A. agilis* on broth agar, on broth gelatin, or in broth without gelatin, the growth is not very vigorous, but the motility is great.

The microscopic appearance of this bactery, in particular of the pure cultures on glucose-agar, is extraordinary. The large, transparent, extremely motile cells, show a wall, a small cell-nucleus, a protoplast with some granules hardly discernible from the nucleus, and often a very distinct vacuole. They measure ca. 5 μ or less, sometimes however more, and are very like small monads, or, when they don't move, like small yeast-cells. At the cell-partition in the living preparation a distinct nucleus-spindle is visible in many cells.

Spores are wanting.

The cilia-coloration is difficult and did not give satisfactory results in my laboratory, I therefore addressed myself, as in the case of *A. chroococcum*, to Professor ZETTNOW in Berlin, to whom I sent *A. agilis*, with a request for his opinion. He had the kindness to supply me with magnificent preparations, which prove most convincingly that the cilia are placed in bundles at the poles. He thereabout writes as follows: „..... In Spirillen-Bouillon [1]) war kein Individuum, das sich nicht auf das lebhafteste bewegt hätte... Nach der Art der ruhigen, wogenden, wenn auch kräftigen Bewegung, welche mich sehr an derjenigen kleiner Monaden erinnerte, hatte ich 1, resp. mehrere Polgeisseln vermuthet, und diese Ansicht haben auch die Preparate aus Spirillen-Bouillon, in welcher die Kultur in vollstem Leben durch Formalin abgetötet wurde bestätigt. Es hat mir jedoch Schwierigkeit gemacht zu diesem Resultat zu kommen. Die 6 bis 10 am Pol, resp. beiden Polen befindlichen Geisseln, legen sich nämlich meistens an der mit vielem stark klebendem Ectoplasma versehenen Oberfläche so an, dass sie scheinbar von der Seite zu entspringen scheinen." I also was at first in doubt and believed to see lateral cilia, but after a minute examination of the preparations I consider Prof. ZETTNOW's description as quite correct.

The relation to nitrogen of *A. agilis* is about the same as in *Azotobacter chroococcum*; to oxygen, on the other hand, it is different, as is proved by the following experiment.

If "respiration figures" [2]) of *agilis* are formed in ordinary microscopic preparations, between object-slide and cover-glass, the most

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[1]) Broth with the addition of 0.1 pCt. KNO^3 and 0.1 pCt. $(NH^4)^2SO^4$.

[2]) For this term to compare: Centralblatt für Bacteriologie Bd. **14**, pag. **827, 1893.**

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strongly motile cells prove, like spirils, to be "mesoaërophilous", but they accumulate somewhat nearer to the meniskus than spirils would do, so that they approach the „macroaërophilous type". When continuing to grow in the glass-room, many cells stick to the glass and then display their mesoaërophilism with great distinctness. *A. chroococcum*, on the other hand, is macroaërophilous.

If the canal-water cultures, with mannite or other sugars as carbon food, are allowed to stand for some weeks at about 18° C., many, but not all, are crowded with an exceedingly rich flora and fauna, so that sugar solutions of 2 pCt. may literally become thick with microbic life, of which, besides *A. agilis* itself, spirils and other bacteria form the main portion, but where amoebae and other protozoa too, are present in great number.

It is a remarkable fact that oligonitrophilism can be the foundation of such a profuseness of life, if only care be taken for sufficient access of air.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents a paper of Dr. C. H. WIND: "*On the irregularities of the cadmium standard cell.*"

1. Some cadmium standard cells constructed in accordance with the directions of the Physikalisch-Technische Reichsanstalt exhibit abnormal phenomena as shown by the observations made in that institution [1]), and also by the researches of COHEN [2]) and others.

COHEN investigated a cell made up as follows:

$$Cd \mid \text{dilute solution of } CdSO_4 \mid \text{Cd-amalgam of } 14.3\ \%,$$

and found in the case of two cells I and II which had been constructed in accordance with this type a difference in EMF. In the cell I it amounted to 56 mV at 0° and to 50 mV at 25°, with an almost linear slope; in cell II it amounted to 51 mV at 0° and to 50 mV at 25°, with a maximum of 52 mV at an intermediate temperature.

COHEN assumes provisionally [3]) that we are dealing here with different modifications or states of equilibrium of the 14.3 per cent amalgam.

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[1]) W. JÄGER u. R. WACHSMUTH — Wied. Ann. 59, p. 575, 1896; W. JÄGER — Wied. Ann. 65, p. 106, 1898; Dr. Ann. 4, p. 123, 1901.

[2]) E. COHEN — Versl. K. A. v. W. Amst. 9, p. 125, 1900.

[3]) id. — L. c. p. 137.

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In fact he found that the cell II after being cooled for the first time from 25° to 0° showed at first a higher EMF (55 mV) which gradually passed into the lower value (51 mV) and that the amalgam I showed a contraction in the dilatometer at 0° while the volume of the amalgam II seemed to remain constant.

From these facts COHEN at first concluded that between 0° and 25° (more correctly 23°) the amalgam I is metastable and the amalgam II stable. Afterwards [1]) he has seen reason to modify this opinion and to look upon I as the stable and on II as the metastable form, although this would render the experience with the dilatometer rather obscure.

In his arguments, COHEN starts from the supposition that the amalgam in both cells had the same quantitative composition and in my opinion it is questionable whether this supposition agrees with the facts. I conceived a doubt about this when reading JÄGER's [2]) note on the dependence of the EMF of the cell

Cd-amalgam 14.3 % | solution of Cd SO_4 | Cd-amalgam x

on the molecular relation x of the mercury to the cadmium in the amalgam which forms the second pole. This research gave me an idea which may perhaps lead to an explanation of the irregularities observed.

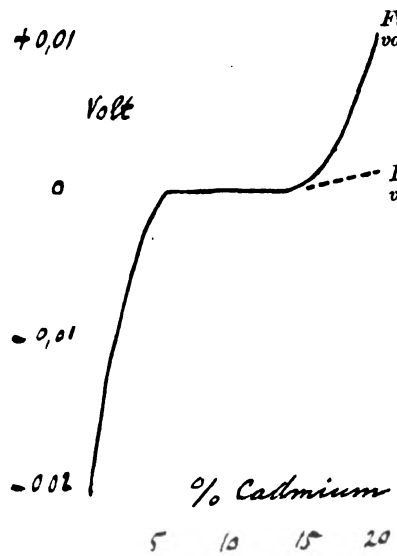

Fig. 1.

2. The curve (fig. 1) representing the EMF of JÄGER's cell in its dependence on the concentration of the variable amalgam pole, shows a part which is parallel to the axis of concentrations: the EMF has proved to be *nil* in the case of all cells with amalgams of 6 to 14,3 % of Cd as second pole.

From the phase rule it may be concluded that the variable amalgam pole will not have been homogeneous in the case of the

[1]) id. — Versl. K. A. v. W. Amst. 9, p. 363, 1900.

[2]) W. JÄGER — Wied. Ann. 65, p. 106, 1898.

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compositions to which this horizontal part of the EMF line relates, but will have consisted of two phases in equilibrium. For it is evident from the course of the above EMF line that in the system Cd-amalgam | solution of $CdSO_4$, if the cadmium content of the amalgam be $> 14{,}3$ or < 6 per cent and the temperature, external pressure and strength of solution are kept constant, one of the variables which, along with those above mentioned, determine the condition of the system must still be arbitrary; because a change in the cadmium content of the amalgam produces a (perfectly definite) change in the potential difference. Under these circumstances there is therefore a complete equilibrium in the system with one arbitrary variable. As there are four independent components (Cd, Hg, $CdSO_4$, H_2O) whilst three of the quantities governing the condition of the system possess a previously given value, there must be $4 + 1 - 3 = 2$ phases in the system. One of those phases is the solution, the other is the amalgam. *Between the above mentioned limits of concentration* the potential difference is, according to JÄGER's measurements, *a perfectly fixed value.* We are consequently dealing *here* with an equilibrium in which none of the quantities determining the condition of the system is arbitrarily variable; the number of phases must have increased by one and the amalgam therefore have split up into two phases. The concentrations of these phases will be the limits of concentration of the region of constant EMF, viz. about 6 and 14.3 percent.

As far as it appears from JÄGER's communications he has not himself drawn these conclusions; nor is it at all sure from what he states that he has noticed any heterogeneities in his amalgams. LINDECK, however, states in an article also cited by JÄGER [1]): „Während bei Amalganen mit hohem Gehalte an Metall Schichten mit verschiedenem spezifischem Gewicht sich manchmal abzusetzen scheinen, ...". DR. E. COHEN, who does not mention anything in his paper about a possible splitting up into two phases, orally communicated to me that he considers this by no means impossible.

Prof. H. W. BAKHUIS ROOZEBOOM informed me that the two-phased equilibrium of cadmium amalgam, the existence of which he had long ago suspected, has been proved in his laboratory in the course of a not yet finished research by Dr. BIJL. Moreover this research has already shown that the limits of concentration for the amalgams, in which that kind of equilibrium is found, are pretty accurately 6 and 14.3 percent of cadmium.

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[1]) S. LINDECK — Wied. Ann. 35, p. 328, 1888.

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3. If we admit the existence of two-phased equilibria in the cadmium amalgams, it is not difficult to suggest causes which may explain the singular phenomena occurring when experimenting with them.

Let us first consider the phenomenon [1]) observed by JÄGER that the EMF of his cell when the second amalgam pole contained 15 percent or more of cadmium, was *nil* immediately after the construction of the cell and arrived at its final value only after the lapse of several hours or even days. The explanation of this phenomenon offers little difficulty, especially when it is taken into consideration that these strong amalgams, as JÄGER observes, are already rather solid so that changes in the distribution of the cadmium can take place but very slowly.

It may be very well imagined that immediately after the construction of the cell, the amalgam poles are not quite homogeneous even when their percentage of cadmium is such that the true equilibrium would consist of one phase only; further that where the amalgam is in contact with the solution of $CdSO_4$ some parts of it are particularly poor in cadmium and may even contain less than 6 percent. If this is really the case, these parts of the surface will possess a greater potential value in reference to the solution than the parts of the surface which are richest in cadmium. This will then cause electric currents in the solution from the richer parts of the surface to the poorer; and these currents will withdraw cadmium from the richer and deposit it on the poorer parts and by this way soon create a condition in which, at the surface layers of the amalgam which are in contact with the solution, no other concentrations occur than such as fall within the region of two-phased equilibria. By all this there will be, however, no equilibrium as yet between those surface layers and the interior of the amalgam with its high percentage of cadmium, and consequently diffusion will occur and in the long run lead to a homogeneous distribution of the cadmium in the amalgam and to a potential difference between amalgam and solution as corresponding to the final equilibrium.

4. The difference observed by COHEN between the two similarly constructed cells I and II (v. § 1) may be readily explained by supposing that COHEN in making the cells unconsciously used portions of a two-phased amalgam. It is then only necessary to assume that

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[1]) L. c. p. 108.

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he happened to use for the cell I a mixture of the two phases in which each of them was present in somewhat considerable quantity and for the cell II a mixture in which the phase containing least cadmium was represented only to a small degree. Indeed if this supposition be true both cells ought at the commencement to show the same EMF, but on cooling to 0° they might behave differently. There are again grounds in this case to expect two distinct states of equilibrium, a *provisional* one, which is established quickly after the lowering of temperature, and a *final* equilibrium, into which the provisional one gradually passes and which will continue to exist as long as the temperature is not again changed. For if the pole of the cell in question is a two-phased amalgam at the higher temperature it will after the fall in temperature still remain heterogeneous at first, while under the influence of local electric currents, as in the case of JÄGER, the potential difference which is established between the amalgam pole and the solution will be the one corresponding to the two-phased equilibrium of the lower temperature. In other words shortly after the fall of temperature we may equally expect in cells I and II the voltage belonging to a two-phased amalgam pole of the new temperature.

What will happen next, depends on the amount of cadmium in the amalgam pole, that is to say on the relative quantities of the two phases in it,and also on the shape of the curve limiting in the diagram of the EMF-isotherms the region of two phases (fig. 2).

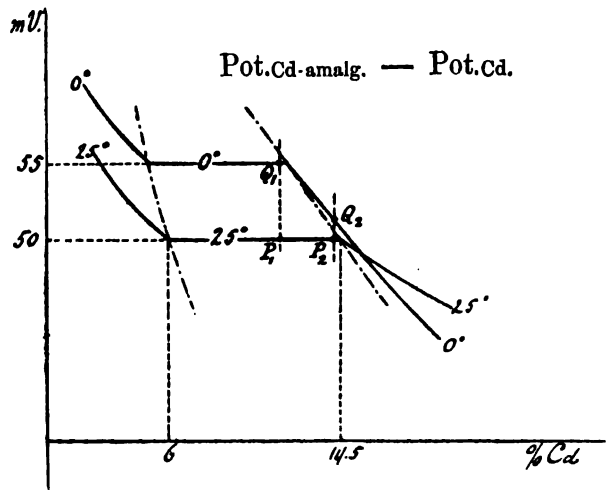

Fig. 2.

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In the case of the amalgam pole I we have assumed that each of the two phases are present in not too small quantities so that the point which indicates its composition on the isotherm of 25° is situated somewhere in P_1 not too near one of the limiting points. The point Q_1 on the isotherm of 0° that lies in the same vertical with P_1 may then easily fall within the region of two phases; it will, however, generally speaking, indicate a considerable change in the ratio of the two phases for the final equilibrium. From this it follows first of all that the potential difference corresponding to the final equilibrium at the lower temperature will not differ from that corresponding to the provisional equilibrium, so that the *final voltage of the cell* will be the same as that shown shortly after the cooling. On the other hand, however, the *final equilibrium* will not be reached until the corresponding ratio of the phases has been fully established in the mixture, a process which will probably be a very slow one. If we now assume that this process is accompanied by contraction, the dilatometric experiment of COHEN with the amalgam I will be fully explained too.

In the case of the amalgam pole II we have assumed that the phase poor in cadmium was present only in a small quantity so that the point P_2 which represents the initial composition of this amalgam lies in the horizontal part of the isotherm of 25° but rather close to one of the limiting points. If we now suppose that here *the curve limiting the region of two phases approaches the EMF-axis as the temperature falls, as indicated in fig.* 2, then the vertical line drawn through P_2 may cut the isotherm of 0° somewhere in a point Q_2 on the descending branch. This point Q_2 gives the EMF belonging to the final equilibrium of the amalgam at 0° and also the nature of this equilibrium. If, therefore, our suppositions are correct, this equilibrium must be one-phased and the final EMF be lower than the one corresponding to the provisional equilibrium.

So it is quite clear why cell II, after cooling to 0° could at first show an EMF of 55 mV and afterwards only one of 51 mV. Whether the limiting curve really takes the above supposed course, may be decided by the experimental investigation of the two-phased region [1]).

Another peculiar fact in COHEN's investigation is this. The cell II, after having been again heated to 25° and having shown there the same EMF as the cell I, when once more cooled to 0° did not

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[1]) From a little sketch forwarded to me a few days ago by Prof. BAKHUIS ROOZEBOOM I think I may conclude that my idea about the course of the limiting curve is correct.

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at first possess the EMF 55 mV, as formerly, but immediately showed the EMF 51 mV [1]). This may be explained by assuming that the amalgam pole after having become homogeneous by the first cooling has remained so when the temperature increased (its state of equilibrium having perhaps been "metastable" towards the end), so that during the subsequent cooling there was not occasion for a distinct provisional equilibrium, as formerly.

5. It appears to me that many of the phenomena observed in the investigation of the WESTON-cell in the Physikalisch-Technische Reichsanstalt which have as yet remained obscure may be explained in an analogous manner by the existence of two-phased equilibria in the cadmium amalgam and by retardations in the attainment of the equilibria.

A result of some practical importance of the above considerations would be, that the Physikalisch-Technische Reichsanstalt by altering their prescription for the construction of cadmium standard cells so as to recommend now a percentage lower than 14.3 of cadmium — whether this was done on sufficient theoretical grounds or not — have found the right way of insuring a cell with a perfectly definite EMF, and so of making the cadmium element more capable of serving as a standard.

Botany. — S. L. SCHOUTEN: "*A pure culture of Saprolegniaceae*". (Communicated by Prof. F. A. F. C. WENT).

A new method which I devised for making pure cultures as well of bacteria as of other micro-organisms and of which a preliminary account appeared in the "Handelingen van het 7de Nederl. Nat. en Geneesk. Congres" amounts essentially to what follows.

On a cover glass, greased with a little vaseline and then passed through a flame 3 or 4 times, a drop is placed in which among others, the micro-organism occurs, which we wish to breed. At a distance of about 2 millimetres another drop is placed of the nutritive fluid in which we will produce the pure culture. Then the cover glass is laid on a moist chamber under the microscope. The right and left sides of this moist chamber have a horizontal slit, closed with olive-oil a little thickened with sulphuret of lead paste. Through

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[1]) E. COHEN — Versl. K. A. v. W. Amst. 9, p. 129, 1900.

[2]) L. c. p. 110.

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the slits 2 glass needles protrude, the ends of which are differently shaped according to the larger or smaller size of the micro-organism to be isolated. By means of a simple mechanism the needles can pivot about a point of support so that their ends can touch the lower surface of the cover glass. Moreover it has been made possible to do this in any place of the field.

On the bottom of the moist chamber a drop of water has been placed beforehand; hence its space is saturated with water vapour. This water vapour is condensed on the lower surface of the cover glass and this having previously been treated with vaseline, the vapour is condensed as small, globular, non-coalescent droplets.

Before being used the needles are sterilised in a way on which we will not dwell here.

Now suppose that we want to isolate a *small* micro-organism e.g. a bacterium. With the strongest magnification (oil-immersion) the edge of the drop, containing the bacteria, is examined. When the bacterium has been found, the needle on the right is moved upwards, so that it reaches the drop close to the bacterium. Now the whole of the moist chamber is moved to the left; to this end it is held in a movable object-stage. By this movement the bacterium together with a very small drop, will be extracted from the large drop. The moist chamber is steadily moved to the left until the small drop with the bacterium in it has come quite near the big drop of nutritive fluid in which the pure culture is to be bred. Now the needle on the right is moved downwards; one makes sure for the last time that no more than that one bacterium has been isolated and then the bacterium and the little drop are carried with the needle on the left into the edge of the big drop in which it is to multiply. The cover glass is then placed on an ordinary moist chamber and allowed to remain for 24 hours at the required temperature. It will appear that in that time a colony has formed at the edge of the drop which may again be examined with the strongest magnification. Bacteria are isolated with a straight, fine-pointed needle.

Larger bacteria e.g. threadshaped ones and other micro-organisms of average size are isolated with a fine inoculating eye; for the largest micro-organisms (such as spores, conidia, zoospores of moulds and algae, myxomycetes, infusoria, yeast-cells, etc.) a coarse open inoculating eye is used. In the latter case we *isolate* with a feebler magnification and only *control* what has been isolated with the strongest magnification. Also in this case the isolated cell is on its way passed through a drop in order to remove any

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bacteria that may accompany it. This drop should be placed between the two others.

I will not dwell on the technical details of the preparation of the needles, on the question why two needles are used, etc. Here I will only give some information about an application of this method, viz. about pure cultures of Saprolegniaceae. These living for the greater part saprophytically, occur mostly in water, teeming with bacteria. Here we have a case in which it is a great advantage to possess a method through which we can isolate under the microscope a single cell (in our case a zoospore) which is not contaminated with bacteria.

A zoospore of Achlya spec. was isolated in an infusion of weevils; after 24 hours it proved to have germinated into a mycelium, occupying nearly the whole drop. This drop with the mycelium was transferred into a tube containing weevil-broth and from this culture inoculations were made on various nutrient materials as weevil-broth with gelatine or agar, pease-water, glucose-peptone (glucose 5 percent, peptone $^1/_2$ percent. potassium phosphate $^1/_{10}$ percent, magnesium sulphate $^1/_{20}$ percent), the same with gelatine or agar, rice, albumen. Less suitable were LÖFFLER's gelatine-broth and agar-broth.

Very little being known about the physiology of nutrition of moulds, living on animal substrata, some points relating to this subject were investigated with Achlya, the more so since the method applied with the same purpose by KLEBS [1]) on Saprolegniaceae, is open to objections.

In order to find out which nitrogenous food is most advantageous for the mould, a number of flasks were provided with a fluid, consisting of 5 percent commercial glucose $^1/_{10}$ percent pot. phosphate and $^1/_{20}$ percent magn. sulphate and so containing all elements excepting N. Then the N-containing food was added to these flasks, a different one to each. To one flask nothing was added. From an experiment of this kind it appeared that sodium nitrite, potassium nitrate and urea were not used as food; the first even acted as a poison. Asparagine was a bad food, amm. sulphate was better, lastly peptone was by far the best.

In a similar way the nutritive value of various C-containing substances was investigated. Here all the flasks were provided with a fluid, consisting of $^1/_2$ percent amm. sulphate (peptone could not

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[1]) Jahrb. für Wiss. Bot. XXXIII pag. 517.

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be used as an N-source, as it also contains C.) $^1/_{10}$ percent pot. phosphate and $^1/_{20}$ percent magn. sulphate. The result was that potato-starch was the best C-food; much less good was maltose and then came in descending order milk-sugar, commercial glucose, syrup of laevulose, cane sugar. Pot. citrate, pot. tartrate, sod. benzoate, sod. butyrate, pot. acetate were not used as food. The last three substances even acted more or less as poisons. Peptone appeared to be both a C- and an N-food. From the group of fats Arachis-oil was chosen for determining its nutritive value. It was not used as food however.

In glucose-peptone the mould causes acid reaction. Bred in anaërobic conditions in the same fluid (by BUCHNER's method) it forms alcohol. From amylum (e. g. in cultures on rice) it forms sugar, dextrine appearing as an intermediate product. This is clearly shown when one follows the auxanographic method of BEIJERINCK-WIJSMAN. An agar-plate, containing $^1/_2$ percent of soluble amylum, is inoculated in the middle with a bit of mycelium. After about 2 days the plate is almost entirely overgrown. A diluted solution of iodine is then poured out over it; that part where the mould has not yet entered or where it is just entering, turns blue; inside the blue one sees a violet-red zone and the large middle part remains colourless.

The fact that the mould liquefies gelatine, made it probable that a proteolytic enzyme would be secreted. The rate at which this enzyme acts and the circumstances under which it is produced, were investigated a little more closely.

At first the method, given by FERMI [1]), was followed. In this method a mixture of 100 c.c. water, 7 grammes of gelatine and 1 gr. of phenol is poured into ordinary test-tubes. After cooling, 2 percent of phenol is added to the liquid the proteolytic enzyme of which one wants to study. Instead of phenol thymol is also prescribed as an antiseptic, otherwise toluene, sodium arsenite etc. One now sees whether the gelatine is liquefied and how soon this takes place. With not very quickly acting enzymes one may have to wait for many days and sometimes weeks before any effect is seen.

Therefore FERMI's method was modified in such a way that the results become visible as soon as possible. To this end one takes water saturated with thymol and adds to it $7^1/_2$ percent of gelatine and so much pounded cinnabar that the liquid looks thoroughly red. This mixture is poured into test-tubes, 5 c.c. into each. When the

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[1]) Arch. f. Hyg. XII, 240.

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gelatine has solidified the tubes are put in a beaker of water, kept at 40° C. The gelatine having melted, the tubes are held for ten seconds in a slanting position under a fan-shaped jet from the water-conduit, which surrounds all the gelatine at once. By this bath of 10 seconds' duration the gelatine does not become solid but viscous. If the tube is thereupon placed vertically, a thin film, of very nearly semi-elliptic form, will remain behind on the wall above the surface of the gelatine. After having cooled, these test-tubes can be filled in the ordinary manner with the fluids we wish to study, with the addition of a little bit of thymol.

The aim of this method is, to bring the enzyme into contact with as large a gelatine-surface as possible. Besides, the gelatine being spread in a very thin layer, it can rapidly be dissolved. By the red colour the liquefaction is sooner observed. The way in which these tubes are prepared, warrants us that the thin layer has the same thickness in all the tubes, which renders a comparative study possible. When the thin film has liquefied, we can by means of the rest of the gelatine at the bottom of the tube, control the action of the enzyme during *longer* periods, as well as in the old method.

With this modified method and at the same time with the old one, the question was studied whether the mould secretes proteolytic enzymes in a nutrient medium of 5 percent albumen in water and in one of glucose-peptone. In both cases the liquid from the culture-flask was used after simple filtration and also a filtered watery infusion of the mycelium crushed with glass-powder.

At 9 o'clock in the evening the experiment was started. The result was already clearly visible the next morning, that is after 12 hours: the thin red layer had almost entirely disappeared in the liquid, obtained from the squeezed mycelium of the albumen-culture and also in the culture-fluid itself; in two similar liquids, obtained from the glucose-peptone culture, the red layer had not yet been noticeably attacked, but only disappeared after $2^1/_2$ days. With the old method no effect was visible after 3 days.

Also during a longer period the action of the enzyme was observed. After 20 days the amount of liquefied gelatine was:

in the albumen-culture liquid	1.75	cc.
„ „ „ „ „ (squeezed mould)	1.55	„
„ „ glucose-peptone-culture liquid	1.10	„
„ „ „ „ „ „ (squeezed mould)	1.00	„

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So we see from this, in accordance with what already appeared from the vanishing of the thin layer, that the enzyme of the albumen-culture acts more energetically than that of the glucose-peptone culture and in both cases we see that the liquid obtained from the squeezed mould-threads contains a less active enzyme than the liquid in which the culture has developed. The enzyme further proved to act in the presence of acid as well as of alkali.

Observations were also made as to whether the mould can, by secreting an enzyme, split up fats into glycerine and free fatty acids. In the culture-flasks a little litmus solution was put, which showed a neutral tint and which accordingly would turn red if such a splitting up took place. The fat chosen was Arachis-oil, which however appeared not to be split up.

It is generally assumed that Saprolegniaceae live saprophytically on animal and vegetable substances, but that they prefer the former. Surely the widely known method for obtaining material of Saprolegniaceae (viz. by throwing weevils or flies into a trough of ditch-water) is one of the causes of this opinion. From the preceding investigations it appears however that we may safely assume vegetable substrata to be at least as advantageous as animal ones. The use of animal substrata for obtaining material finds a probable explanation in the fact that there are relatively few moulds, which live saprophytically on animals, so that other undesirable fungi will not easily develop on those animals.

(April 23, 1901).

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday April 20, 1901.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 20 April 1901, Dl. IX).

CONTENTS: Prof. H. A. LORENTZ: "BOLTZMANN's and WIEN's Laws of radiation", p. 607. — Prof. H. KAMERLINGH ONNES and H. H. FRANCIS HYNDMAN: "Isothermals of diatomic gases and their binary mixtures. I. Piezometers of variable volume for low temperatures", p. 621, (with 2 plates). — Prof. H. KAMERLINGH ONNES: "On DE HEEN's experiments about the critical state", p. 628. — Prof. J. D. VAN DER WAALS: "The equation of state and the theory of cyclic motion" III, p. 643. — Prof. J. L. C. SCHROEDER VAN DER KOLK: "On hardness in minerals in connection with cleavage" p. 655. — Prof. J. C. KAPTEYN: "On the luminosity of the fixed stars", p. 658. — H. D. BEYERMAN: "On the influence upon respiration of the faradic stimulation of nerve tracts passing through the internal capsula", (Communicated by Prof. C. WINKLER), (with 1 plate) p. 689. — Prof. H. KAMERLINGH ONNES: "On differences of density in the neighbourhood of the critical state arising from differences of temperature", p. 691. — Prof. JAN DE VRIES: "Involutions on a curve of order four with triple point". p. 696. — Dr. F. A. H. SCHREINEMAKERS: "Notes on equilibria in ternary systems", (Communicated by Prof. J. M. VAN BEMMELEN), p. 701. — Dr. P. K. LULOFS: "Substitution velocity in the case of aromatic halogen-nitroderivatives", (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 715. — Dr. A. SMITS: "On the progressive change of the factor i as function of the concentration". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 717.

The following papers were read:

Physics. — Prof. H. A. LORENTZ: "BOLTZMANN's *and* WIEN's *Laws of Radiation.*"

(Read February 23, 1901)

The theoretical proof of the laws, to which BOLTZMANN [1]) and WIEN [2]) have been led by the application of thermodynamics to the phenomena of radiation may be made to depend directly on the equations of the electromagnetic field, a method which has the

[1]) BOLTZMANN, Wied. Ann. Bd. 22, p. 291; 1884.

[2]) WIEN, Berliner Sitz. Berichte, 1893, p. 55.

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advantage that the notion of "rays" of light and heat is almost wholly avoided.

§ 1. Let us consider a space, enclosed by walls that are perfectly reflecting on the inside, and containing a ponderable body M, the remaining part being occupied by aether. In this medium we shall then have a state of radiation, the nature of which is determined by the temperature T of the body M; in virtue of this state the aether will exert on the reflecting walls a certain pressure, the amount of which for unit area we shall denote by p. Let v be the volume within the enclosure. It may be enlarged or diminished by a displacement of the walls. We shall also suppose that by some means or other heat may be imparted to the body M.

Now, choosing v and T as independent variables, and denoting by ε the energy of the whole system, we shall have

$$dQ = \frac{\partial \varepsilon}{\partial T} dT + \left(\frac{\partial \varepsilon}{\partial v} + p \right) dv$$

for the heat that is required for the infinitesimal change, determined by dT and dv, and, by the rule that $\frac{dQ}{T}$ is an exact differential,

$$\frac{\partial \varepsilon}{\partial v} + p = T \frac{\partial p}{\partial T}.$$

Here the first term represents the energy of the aether per unit volume, which we shall call U. Indeed, if we increase the volume v, keeping the temperature constant, the ponderable body will remain in the same state (the pressure p exerted on this body by the surrounding aether will not be altered, being a function of T alone); the increment of ε will therefore be the energy contained in the new part that is added to v. Hence

$$U + p = T \frac{dp}{dT}, \quad \ldots \ldots \ldots \quad (1)$$

the last term containing an ordinary differential coefficient, because p is independent of v.

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§ 2. We shall combine this result with the simple relation

$$p = \frac{1}{3} U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which we now proceed to prove. To this effect we remember in the first place that the energy per unit volume is given by [1])

$$2\pi V^2 \mathfrak{d}^2 + \frac{1}{8\pi} \mathfrak{H}^2.$$

We shall therefore write

$$U = 2\pi V^2 \overline{\mathfrak{d}^2} + \frac{1}{8\pi} \overline{\mathfrak{H}^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the horizontal bars indicating mean values with respect to place and time, which we might calculate by computing in the first place the mean values for all points of a certain space, and by taking then, for a certain lapse of time, the mean of these space-means. In this it is to be understood that the dimensions of the space in question and the length of the lapse of time have to be large, as compared with the wave-length and the time of vibration.

If we confine ourselves to such mean values, the forces acting on the walls may be regarded as due to a state of stress in the aether. If α, β and γ are the direction-cosines of the normal n of an element of surface, the first component of the stress on this element will be

$$X_n = 2\pi V^2 (2 \overline{\mathfrak{d}_x \mathfrak{d}_n} - \alpha \overline{\mathfrak{d}^2}) + \frac{1}{8\pi} (2 \overline{\mathfrak{H}_x \mathfrak{H}_n} - \alpha \overline{\mathfrak{H}^2});$$

i.e., this will be the force in the direction of OX, exerted by the part of the medium which lies on the side of the element, indicated by the normal n.

Now, the state of radiation we are considering has the same properties in all directions. From this it follows that there are no tangential stresses and that the normal stress is the same for all directions of the element of surface. It is given by

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[1]) The notation is the same as in my »Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern", from which memoir I have also borrowed several formulae.

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$$X_x = 2\pi V^2 (2\overline{\mathfrak{d}_x^2} - \overline{\mathfrak{d}^2}) + \frac{1}{8\pi}(2\overline{\mathfrak{H}_x^2} - \overline{\mathfrak{H}^2}).$$

But, in an isotropic state,

$$\overline{\mathfrak{d}_x^2} = \overline{\mathfrak{d}_y^2} = \overline{\mathfrak{d}_z^2}, \qquad \overline{\mathfrak{H}_x^2} = \overline{\mathfrak{H}_y^2} = \overline{\mathfrak{H}_z^2}.$$

Therefore:

$$\overline{\mathfrak{d}_x^2} = \frac{1}{3}\overline{\mathfrak{d}^2}, \qquad \overline{\mathfrak{H}_x^2} = \frac{1}{3}\overline{\mathfrak{H}^2},$$

and

$$X_x = -\frac{2}{3}\pi V^2 \overline{\mathfrak{d}^2} - \frac{1}{24\pi}\overline{\mathfrak{H}^2}.$$

In comparing this formula, in which the negative sign indicates a *pressure*, with (3), we arrive at the relation (2).

In virtue of this the equation (1) now takes the form:

$$4U = T\frac{dU}{dT},$$

and so we find the law, enunciated by BOLTZMANN, that the energy U per unit volume is proportional to the fourth power of the absolute temperature.

§ 3. If the volume v is increased, the system will do an external work and a larger volume of aether will be filled with the energy of radiation; for both reasons the temperature of the body M will sink, if the operation is conducted adiabatically. We may also, before increasing the volume, remove the body M; in this case we start from a volume v of aether in the particular state of radiation that corresponds to the temperature T, and we get new states by letting the walls recede with a velocity which we shall suppose to be extremely small in comparison with the velocity of light. Now WIEN has shown in the first place, by a train of thermodynamical reasoning, that these new states, of smaller energy-density than the original one, are precisely such as can be in equilibrium with ponderable bodies of temperatures lower than T. Using BOLTZMANN's law, we may express this as follows: After having diminished, by means of an adiabatic expansion, the energy per unit volume from U to U', we shall have arrived at a state

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of radiation which may be in equilibrium with a ponderable body of the temperature

$$T' = T\sqrt[4]{\frac{U'}{U}}.$$

This theorem, which I shall here admit without further discussion, enables us to determine the relation between the states of radiation corresponding to the temperatures T and T'. For this purpose it will only be necessary to compare the states of the aether before and after the expansion. This is the second part of the proof given by WIEN, and it is this part we shall present in a modified form by applying the well known equations of the electromagnetic field to the phenomena in the aether within the receding walls. If we suppose the expanding enclosure to remain geometrically similar to itself, the problem may be treated by the introduction of a suitable set of new variables. In seeking for these, I have kept in mind the substitutions that had proved of use in the theory of aberration, a theory in which we have likewise to do with moving ponderable bodies. Of course there is a difference between the two cases; in the problem of aberration the velocity is the same for all bodies concerned, whereas, in the question now under consideration, it is unequal for different points of the enclosures.

§ 4. I shall suppose the dilatation of the walls to be equal in all directions, and to have the same amount in equal infinitely small times. This may be expressed by assuming

$$x = x' e^{at},\ y = y' e^{at},\ z = z' e^{at}, \quad \ldots\ldots \quad (4)$$

with a constant value of a, as the relation between the coordinates x, y, z of a point of the walls at time t, and the coordinates x', y', z' of the same point at the instant $t = 0$, at which we begin to consider the phenomena. Indeed, the velocities are by (4)

$$ax,\ ay,\ az; \quad \ldots\ldots\ldots \quad (5)$$

during the time dt the linear dimensions will therefore be changed in the ratio of 1 to $1 + adt$.

As to the constant a, we shall take it so small that the velocities (5) are extremely small in comparison with the velocity of light. Notwithstanding this we may, by sufficiently increasing t, assign to the factor e^{at} any value we like.

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After having assumed for the walls the formulae (4), it is natural to replace the coordinates x, y, z of any point of the enclosed space by the new variables

$$x' = x\,e^{-at},\quad y' = y\,e^{-at},\quad z' = z\,e^{-at}. \quad . \quad . \quad . \quad . \quad (6)$$

The fourth independent variable, the time t, will likewise be replaced by a new one. For this we take [1])

$$t' = \frac{1}{a}(1-e^{-at}) - \frac{a}{2\,V^2}(x^2+y^2+z^2)\,e^{-at}. \quad . \quad . \quad . \quad (7)$$

The dependent variables which occur in the equations of the electromagnetic field are now to be considered as functions of x', y', z', t'. In doing so, we have to use the relations

$$\left.\begin{aligned} \frac{\partial}{\partial x} &= e^{-at}\frac{\partial}{\partial x'} - \frac{ax}{V^2}e^{-at}\frac{\partial}{\partial t'},\\ \frac{\partial}{\partial y} &= e^{-at}\frac{\partial}{\partial y'} - \frac{ay}{V^2}e^{-at}\frac{\partial}{\partial t'},\\ \frac{\partial}{\partial z} &= e^{-at}\frac{\partial}{\partial z'} - \frac{az}{V^2}e^{-at}\frac{\partial}{\partial t'}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\frac{\partial}{\partial t} = e^{-at}\left[1+\frac{a^2}{2\,V^2}(x^2+y^2+z^2)\right]\frac{\partial}{\partial t'} -$$

$$- ax\,e^{-at}\frac{\partial}{\partial x'} - ay\,e^{-at}\frac{\partial}{\partial y'} - az\,e^{-at}\frac{\partial}{\partial z'}. \quad . \quad . \quad . \quad (9)$$

The variables which serve to determine the state of the aether are $\mathfrak{d}_x$, $\mathfrak{d}_y$, $\mathfrak{d}_z$, $\mathfrak{H}_x$, $\mathfrak{H}_y$, $\mathfrak{H}_z$. We shall replace these by the quantities $\mathfrak{d}'_x$, $\mathfrak{d}'_y$, $\mathfrak{d}'_z$, $\mathfrak{H}'_x$, $\mathfrak{H}'_y$, $\mathfrak{H}_z'$, which are defined by the following equations [2])

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[1]) As regards the last term, this value of t' is an imitation of the expression for the "local time", which I have introduced into the theory of aberration (l. c. p. 49).

[2]) The latter terms in these equations correspond to similar terms in the equations of the theory of aberration.

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$$\left.\begin{aligned} \mathfrak{d}_x &= e^{-2at}\,\mathfrak{d}'_x - \frac{a}{4\pi V^2}(y\,\mathfrak{H}_z - z\,\mathfrak{H}_y), \\ \mathfrak{d}_y &= e^{-2at}\,\mathfrak{d}'_y - \frac{a}{4\pi V^2}(z\,\mathfrak{H}_x - x\,\mathfrak{H}_z), \\ \mathfrak{d}_z &= e^{-2at}\,\mathfrak{d}'_z - \frac{a}{4\pi V^2}(x\,\mathfrak{H}_y - y\,\mathfrak{H}_x), \end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

$$\left.\begin{aligned} \mathfrak{H}_x &= e^{-2at}\,\mathfrak{H}'_x + 4\pi a\,(y\,\mathfrak{d}_z - z\,\mathfrak{d}_y), \\ \mathfrak{H}_y &= e^{-2at}\,\mathfrak{H}'_y + 4\pi a\,(z\,\mathfrak{d}_x - x\,\mathfrak{d}_z), \\ \mathfrak{H}_z &= e^{-2at}\,\mathfrak{H}'_z + 4\pi a\,(x\,\mathfrak{d}_y - y\,\mathfrak{d}_x). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (11)$$

It must be kept in mind that the coefficient a is very small. Let l be the largest value of any dimension of the system during the interval of time we wish to consider. Then, by our assumption,

$$\frac{a\,l}{V}$$

has a very small value $\varkappa$; evidently, $\frac{ax}{V}$, $\frac{ay}{V}$, $\frac{az}{V}$ will be of the same order of magnitude. Hence, if we neglect quantities which, compared with other terms in the same equation, are of the order $\varkappa^2$, we may omit in (9) the term containing a^2. By this, the relation becomes

$$\frac{\partial}{\partial t} = e^{-at}\frac{\partial}{\partial t'} - ax\,e^{-at}\frac{\partial}{\partial x'} - ay\,e^{-at}\frac{\partial}{\partial y'} - az\,e^{-at}\frac{\partial}{\partial z'}. \quad . \quad . \quad (9')$$

We may add that for vibratory disturbances of the natural state of the aether, the operations $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, $\frac{\partial}{\partial z}$ are comparable to $\frac{1}{V}\frac{\partial}{\partial t}$, as regards the order of magnitude of the result, and that $\mathfrak{H}$ is of the same order as $V\mathfrak{d}$. From this it follows that, in the equations (8), (9'), (10) and (11), all terms containing the factor a are of the order $\varkappa$, relatively to the terms in which a does not occur. Similarly, attentive consideration of the formulae that will be deduced in the next article shows that, in comparison with the terms without a, all those which contain the factor a^2 are of the order $\varkappa^2$. We shall therefore neglect all terms in which a^2 appears.

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§ 5. The first equation of motion is:

$$\frac{\partial \mathfrak{H}_z}{\partial y} - \frac{\partial \mathfrak{H}_y}{\partial z} = 4\pi \frac{\partial \mathfrak{d}_x}{\partial t}. \quad \ldots \ldots \quad (12)$$

Putting for $\mathfrak{H}_y$ and $\mathfrak{H}_z$ the values (11), we find for its left-hand side:

$$e^{-2at}\left(\frac{\partial \mathfrak{H}'_z}{\partial y} - \frac{\partial \mathfrak{H}'_y}{\partial z}\right) + 4\pi a\left(x\frac{\partial \mathfrak{d}_y}{\partial y} - y\frac{\partial \mathfrak{d}_x}{\partial y} - \mathfrak{d}_x\right) -$$

$$- 4\pi a\left(z\frac{\partial \mathfrak{d}_x}{\partial z} - x\frac{\partial \mathfrak{d}_z}{\partial z} + \mathfrak{d}_x\right).$$

Since

$$\frac{\partial \mathfrak{d}_x}{\partial x} + \frac{\partial \mathfrak{d}_y}{\partial y} + \frac{\partial \mathfrak{d}_z}{\partial z} = 0,$$

we may also write for it

$$e^{-2at}\left(\frac{\partial \mathfrak{H}'_z}{\partial y} - \frac{\partial \mathfrak{H}'_y}{\partial z}\right) - 8\pi a \mathfrak{d}_x - 4\pi a\left(x\frac{\partial \mathfrak{d}_x}{\partial x} + y\frac{\partial \mathfrak{d}_x}{\partial y} + z\frac{\partial \mathfrak{d}_x}{\partial z}\right),$$

and, if we neglect terms with a^2,

$$e^{-2at}\left(\frac{\partial \mathfrak{H}'_z}{\partial y} - \frac{\partial \mathfrak{H}'_y}{\partial z}\right) - 8\pi a e^{-2at}\mathfrak{d}'_x -$$

$$- 4\pi a e^{-3at}\left(x\frac{\partial \mathfrak{d}'_x}{\partial x'} + y\frac{\partial \mathfrak{d}'_x}{\partial y'} + z\frac{\partial \mathfrak{d}'_x}{\partial z'}\right). \quad \ldots \quad (13)$$

Again, using the same simplification,

$$\frac{\partial}{\partial y} = e^{-at}\frac{\partial}{\partial y'} - \frac{ay}{V^2}\frac{\partial}{\partial t},$$

$$\frac{\partial}{\partial z} = e^{-at}\frac{\partial}{\partial z'} - \frac{az}{V^2}\frac{\partial}{\partial t},$$

$$\frac{\partial \mathfrak{H}'_z}{\partial y} - \frac{\partial \mathfrak{H}'_y}{\partial z} = e^{-at}\left(\frac{\partial \mathfrak{H}'_z}{\partial y'} - \frac{\partial \mathfrak{H}'_y}{\partial z'}\right) - \frac{a}{V^2}\left(y\frac{\partial \mathfrak{H}'_z}{\partial t} - z\frac{\partial \mathfrak{H}'_y}{\partial t}\right).$$

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In the last term of this equation, $\frac{\partial \mathfrak{H}'_y}{\partial t}$ and $\frac{\partial \mathfrak{H}'_z}{\partial t}$ may be replaced by $e^{2at}\frac{\partial \mathfrak{H}_y}{\partial t}$ and $e^{2at}\frac{\partial \mathfrak{H}_z}{\partial t}$, as appears from (11). The expression (13) therefore becomes

$$e^{-3at}\left(\frac{\partial \mathfrak{H}'_z}{\partial y'} - \frac{\partial \mathfrak{H}'_y}{\partial z'}\right) - \frac{a}{V^2}\left(y\frac{\partial \mathfrak{H}_z}{\partial t} - z\frac{\partial \mathfrak{H}_y}{\partial t}\right) -$$

$$- 8\pi a e^{-2at}\mathfrak{d}'_x - 4\pi a e^{-3at}\left(x\frac{\partial \mathfrak{d}'_x}{\partial x'} + y\frac{\partial \mathfrak{d}'_x}{\partial y'} + z\frac{\partial \mathfrak{d}'_x}{\partial z'}\right). \quad (14)$$

The right-hand side of (12) is, by (10),

$$- 8\pi a e^{-2at}\mathfrak{d}'_x + 4\pi e^{-2at}\frac{\partial \mathfrak{d}'_x}{\partial t} - \frac{a}{V^2}\left(y\frac{\partial \mathfrak{H}_z}{\partial t} - z\frac{\partial \mathfrak{H}_y}{\partial t}\right),$$

or, if (9′) is taken into account,

$$- 8\pi a e^{-2at}\mathfrak{d}'_x + 4\pi e^{-3at}\frac{\partial \mathfrak{d}'_x}{\partial t'} -$$

$$- 4\pi a e^{-3at}\left(x\frac{\partial \mathfrak{d}'_x}{\partial x'} + y\frac{\partial \mathfrak{d}'_x}{\partial y'} + z\frac{\partial \mathfrak{d}'_x}{\partial z'}\right) -$$

$$- \frac{a}{V^2}\left(y\frac{\partial \mathfrak{H}_z}{\partial t} - z\frac{\partial \mathfrak{H}_y}{\partial t}\right). \quad . \quad . \quad . \quad (15)$$

Finally we shall find, instead of (12), after division by e^{-3at},

$$\frac{\partial \mathfrak{H}'_z}{\partial y'} - \frac{\partial \mathfrak{H}'_y}{\partial z'} = 4\pi\frac{\partial \mathfrak{d}'_x}{\partial t'}.$$

The other equations may be treated in the same way and all relations between the new variables will be found to be of the same form as those between the original ones.

§ 6. We have also to attend to the surface conditions at the walls. These latter will be perfectly reflecting, if made of a substance of infinite specific inductive capacity, and then, if the wall is at rest, the tangential components of the dielectric displacement in the adjacent aether will be zero. Therefore, if

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$$F(x, y, z) = 0 \quad \ldots\ldots\ldots \quad (16)$$

is the equation of the wall, we shall have

$$\mathfrak{d}_x : \mathfrak{d}_y : \mathfrak{d}_z = \frac{\partial F}{\partial x} : \frac{\partial F}{\partial y} : \frac{\partial F}{\partial z}. \quad \ldots\ldots \quad (17)$$

In examining the phenomena of aberration, I have had occasion to consider the conditions that have to be fulfilled at the surface of separation of two bodies. These latter were supposed to move with a common velocity $\mathfrak{p}$, and it was found that all equations, the surface conditions as well as those for the interior of the bodies, might, by an appropriate choice of new variables, be reduced to the form that holds in the case of bodies at rest. Instead of the dielectric displacement with the components

$$\mathfrak{d}_x, \ \mathfrak{d}_y, \ \mathfrak{d}_z \ , \quad \ldots\ldots\ldots \quad (18)$$

a new vector with the components

$$\left.\begin{aligned} &\mathfrak{d}_x + \frac{1}{4\pi V^2}(\mathfrak{p}_y \mathfrak{H}_z - \mathfrak{p}_z \mathfrak{H}_y), \\ &\mathfrak{d}_y + \frac{1}{4\pi V^2}(\mathfrak{p}_z \mathfrak{H}_x - \mathfrak{p}_x \mathfrak{H}_z), \\ &\mathfrak{d}_z + \frac{1}{4\pi V^2}(\mathfrak{p}_x \mathfrak{H}_y - \mathfrak{p}_y \mathfrak{H}_x) \end{aligned}\right\} \quad \ldots\ldots \quad (19)$$

was introduced. Hence, it will be this new vector, whose tangential components must vanish at a moving perfectly reflecting surface.

Let us apply this rule to an element of the walls of the expanding enclosure. The velocity-components $\mathfrak{p}_x$, $\mathfrak{p}_y$, $\mathfrak{p}_z$ must now be replaced by $a\,x$, $a\,y$, $a\,z$. Using at the same time the formulae (10), we find for the expressions (19)

$$e^{-2at}\mathfrak{d}'_x, \ e^{-2at}\mathfrak{d}'_y, \ e^{-2at}\mathfrak{d}'_z.$$

It thus appears that the vector

$$e^{-2at}\mathfrak{d}'$$

must be perpendicular to the wall. The vector $\mathfrak{d}'$ must be so

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likewise, so that, if at any moment

$$F'(x, y, z) = 0$$

is the equation of the walls, we shall have

$$\mathfrak{d}'_x : \mathfrak{d}'_y : \mathfrak{d}'_z = \frac{\partial F'}{\partial x} : \frac{\partial F'}{\partial y} : \frac{\partial F'}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Now, if at the instant $t = 0$, the walls coincide with the surface determined by (16), the equation at any later time will be

$$F(x', y', z') = 0,$$

where

$$x' = x e^{-at}, \; y' = y e^{-at}, \; z' = z e^{-at},$$

agreeing with (4). Thus:

$$F'(x, y, z) = F(x', y', z'),$$

and, if we differentiate for a constant t,

$$\frac{\partial F'}{\partial x} : \frac{\partial F}{\partial y} : \frac{\partial F'}{\partial z} = \frac{\partial F}{\partial x'} : \frac{\partial F}{\partial y'} : \frac{\partial F}{\partial z'},$$

so that the surface conditions become

$$\mathfrak{d}'_x : \mathfrak{d}'_y : \mathfrak{d}'_z = \frac{\partial F}{\partial x'} : \frac{\partial F}{\partial y'} : \frac{\partial F}{\partial z'} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

On the right-hand side of this formula, x', y', z' occur in exactly the same manner as x, y, z in the formula (17).

§ 7. If the enclosure were permanently in the position it occupies at the time $t = 0$, $\mathfrak{d}_x$, $\mathfrak{d}_y$, $\mathfrak{d}_z$, $\mathfrak{H}_x$, $\mathfrak{H}_y$, $\mathfrak{H}_z$ would be certain functions of x, y, z, t, say

$$\mathfrak{d}_x = \varphi_1(x, y, z, t), \; \mathfrak{H}_x = \chi_1(x, y, z, t), \text{ etc.}; \quad . \quad . \quad (22)$$

these will satisfy both the equations of the field and the surface conditions (17).

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Now, from all that has been said, it appears that the values

$$\mathfrak{d}'_x = \varphi_1(x', y', z', t'),\ \mathfrak{H}_x' = \chi_1(x', y', z', t'),\ \text{etc.} \ldots \quad (23)$$

will be a solution of the equations of the field, taken conjointly with the conditions (21), we have found for the receding walls. We have thus got expressions representing the state of the aether during the expansion.

Now, we shall especially consider the state of things, existing at the moment when the dimensions have become

$$e^{at} = k$$

times what they were originally. A definite value of this coefficient k may be reached in a shorter or a longer time, this depending on the value of a. We shall however consider the limit to which the state of the aether tends, if, while we keep k fixed, t is continually increased and a continually diminished. By (10) and (11) we shall have ultimately

$$\mathfrak{d} = \frac{\mathfrak{d}'}{k^2},\ \text{and}\ \mathfrak{H} = \frac{\mathfrak{H}'}{k^2};$$

therefore, at the limit,

$$\mathfrak{d}_x = \frac{1}{k^2}\varphi_1\left(\frac{x}{k}, \frac{y}{k}, \frac{z}{k}, t'\right),\ \mathfrak{H}_x = \frac{1}{k^2}\chi_1\left(\frac{x}{k}, \frac{y}{k}, \frac{z}{k}, t'\right),\ \text{etc.} \quad (24)$$

As to the variable t', it is related to t in a somewhat complicated manner; the relation between the differentials takes however the simple form

$$dt' = \frac{1}{k}dt.$$

It is easily seen that the function (24) will satisfy the surface conditions such as they are for walls that are kept at rest. This is what we might have expected. By sufficiently diminishing the velocity of the walls, we make the system pass through a series of successive states that may, each of them, be regarded as a state of equilibrium. By WIEN's principle (§ 3) we know already that each of these states might continue to exist if the enclosure contained a ponderable body of a definite temperature.

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The series starts with the state (22), with which (24) coincides if $k = 1$; it then passes to increasing values of k.

We shall denote by T the temperature of a ponderable body that may be in equilibrium with (22), and by T' the corresponding temperature for (24).

§ 8. Let us now compare the states (22) and (24). At first sight there is a difficulty in as much as the variables t and t' have widely different values. It is to be borne in mind, however, that the state (22) is a *stationary* one; i. e. all particulars that may be deduced from observation are independent of the time t.

We may therefore begin by choosing the instant for which we wish to consider the state (24); a definite value having in this way been assigned to t', we may give an equal value to the time t in (22). In other words, we shall compare the quantities (24) with the values

$$\mathfrak{d}_x = \varphi_1(x, y, z, t'), \quad \mathfrak{H}_x = \chi_1(x, y, z, t'), \text{ etc., } \ldots \quad (25)$$

the latter state existing in a certain space S, and the former in a space S', whose dimensions are k times as great.

The values of $\mathfrak{d}$ and $\mathfrak{H}$ in corresponding points of S and S' are to each other as 1 to $\frac{1}{k^2}$, and the energy per unit volume will be in (24) k^4 times smaller than in (25). Hence, remembering BOLTZMANN'S law,

$$T' = \frac{T}{k}. \quad \ldots \quad (26)$$

In examining the phenomena, represented by (25), it may be convenient to decompose, by means of FOURIER'S theorem, or otherwise, the values (25) into functions of x, y, z of a less complicated form. After having accomplished such a decomposition for (25), a similar development of (24) may at once be written down. For instance, if

$$\psi_1(x, y, z, t')$$

is one of the parts of $\mathfrak{d}_x$ in (25), the corresponding part in (24) will be

$$\frac{1}{k^2}\,\psi_1\left(\frac{x}{k}, \frac{y}{k}, \frac{z}{k}, t'\right).$$

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There is also a simple relation between the space-variations in the two cases. Let $P\,Q$ and $P'\,Q'$ be corresponding lines in S and S'. Then, if we denote by η one of the components of $\mathfrak{d}$ or $\mathfrak{H}$, and by η_P, η_Q, $\eta_{P'}$, $\eta_{Q'}$ its values in the points considered, we shall have

$$\frac{\eta_Q - \eta_P}{\eta_P} = \frac{\eta_{Q'} - \eta_{P'}}{\eta_{P'}} ;$$

i. e. the relative variations along corresponding lines will be equal.

From this it is immediately seen that, if one of the parts into which we have decomposed (25) is characterized by a definite wave-length l, the corresponding part of (24) will have a wave-length

$$l' = kl.$$

Therefore

$$l : l' = T' : T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

i. e. corresponding wave-lengths in the two states are to each other in the inverse ratio of the temperatures.

We have already spoken of the ratio between the values of the energy per unit volume. We may add that this ratio, equal to that of the fourth powers of the temperatures, does not only hold for the really existing states of motion, but also for the parts into which these may be decomposed in the way that has been indicated. If, in the state corresponding to the temperature T, there is a certain amount of energy u per unit volume, depending on the vibrations whose wave-lengths lie between certain limits, and if, in the state for which the temperature is T', u' is the energy per unit volume due to the vibrations of corresponding wave-lengths, we shall have

$$u : u' = T^4 : T'^4.$$

This equation, taken together with (27), is the expression of the law of WIEN.

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Physics. — Dr. KAMERLINGH ONNES and H. H. FRANCIS HYNDMAN: „*Isothermals of diatomic gases and their binary mixtures. I. Piezometers of variable volume for low temperatures.*" (Communications from the Physical Laboratory at the University of Leiden. No. 69.)

(Read March 30, 1901).

§ 1. On theoretical grounds, for accurate measurements on the isothermals of pure gases and their binary mixtures, we should have preferred to use monatomic gases alone since results obtained from them would certainly be the most important.

Unfortunately of the three monatomic gases available for this kind of work i. e. He, A, Hg, the two first are costly and the latter has a critical temperature so high that the research would offer great experimental difficulties.

From these we naturally turn to the next group, that of the diatomic gases. Very complete researches on these gases have been made at temperatures above 0° C. and with pressures up to 3000 At. especially by AMAGAT. At low temperatures however no data exist with the exception of two pioneer researches by v. WROBLEWSKI [1]) on Hydrogen down to — 180° C. and by WITKOWSKI [2]) on air down to — 145° C.

The series of experiments which we now consider has been before alluded to in Comm. No. 14 p. 4, 1894 and Comm. No. 50 p. 4, 1899 and has been kept in view in the arrangement of the cryogenic laboratory with its auxiliary apparatus as weli as for the standard manometers. (Comms. 44 and 50.)

In order to obtain the required data two methods present themselves. In the first a constant volume is filled at a constant measurable temperature and pressure by compressed gas which is afterwards expanded so that its volume can be obtained under normal conditions. This method has been used by REGNAULT, v. WROBLEWSKI and WITKOWSKI and where the purity of the gas is not of the greatest importance and especially at high temperatures it is excellent, but to arrive at high precision piezometers of a relatively considerable volume are necessary. Since the piezometer must be refilled for every measurement, somewhat considerable quantities of compressed gas are required for a series of measurements. For determinations in the neighbourhood of the critical point however

[1]) Wien Sitz. Ber. 1888.

[2]) Bull. Int. Acad. Cracovie Mai 1891.

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it is absolutely necessary to employ only gas of the greatest purity to obtain any definite results. A method which requires large volumes of such gas is necessarily both troublesome and costly, so that we have been obliged to introduce some modifications and additions. Of these the most important is a compression cylinder in which the gas after expansion to normal volume can be collected and compressed again into the piezometer, without any loss of purity. However even with this modification a considerable volume of compressed gas is required to fill the piezometer and the necessary connecting tubes. In subsequent communications we will consider the application of this modified method for measurements in the critical region and of a higher accuracy than we are concerned with below.

In the second method, which we are employing for the present investigation because of its relative simplicity, we use a piezometer of variable volume in which a quantity of gas that has once been measured under normal conditions is employed for a series of determinations. In principle this method is an adaptation of the one described in Comm. N° 50 with which SCHALKWIJK has determined the isothermal of Hydrogen at 20° C.

The results of these measurements which will soon be published show that the method is capable of great accuracy under these advantageous circumstances, but we have been unable to maintain this high standard in modifying it for low temperatures. A consideration of the various difficulties to be surmounted in the apparatus we shall describe and the unavoidable errors belonging thereto, show that an accuracy of $\frac{1}{1000}$ is not of easy attainment and that very special apparatus, again of large volume, would be required to reach a higher degree.

This accuracy is not sufficient to determine the deviations of the hydrogen isotherms from the law of corresponding states relatively to other gases, for it follows from the available data that unless constant temperatures of below 200° C or very high pressures are employed determinations to this accuracy will not teach us much on the most important questions.

However with the other gases of this group and especially for a review of the relations between Oxygen and Nitrogen and their mixtures this accuracy may be considered to be sufficient.

§ 2. *General arrangement.* The apparatus which is in use for these measurements has been designed to allow of the determination

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of volume in a room where the liquid gases to produce the low temperature baths can be most readily obtained, and of the pressure in the room containing the precision piezometers and standard manometer. The pressure has thus to be transferred for a distance of some 25 meters by a tube filled with compressed air. The general arrangement of the apparatus is shown diagrammatically in Plate I where the manometer (cf. § 5), is not drawn. The steel cylinder A is connected to the reservoir C and the level tube C_3 (cf. § 3) by steel tubes of 2 mm. bore provided for manipulation with steel cocks C_5 and C_6 of the type given in Comm. N° 46 fig. 10. Dry air under pressure is admitted at the brass cock C_7 its approximate pressure being read by the operating metal manometer M while its actual pressure is determined by the gas manometer (cf. § 5) connected at C_8. The cock C_9 is for emergency and for reducing the pressure and C_{10}, C_{11} for manipulation.

The washers at the numerous joints are all of prepared leather and require much trouble and attention before they are quite tight, though this is now satisfactorily attained.

§ 3. *The Piezometer.* Although the principle of the method employed is the same as that described in Comm. N°. 50 many modifications are necessary to adapt it for measurements at temperatures below the freezing point of mercury. The simplest would be to separate the bath and graduated tube by a long fine glass capillary bent twice at right angles so that the bulb could be immersed in the low temperature bath while the graduated tube remained at an ordinary constant temperature. Such a rigid connection would give much difficulty in manipulation and would be liable to fracture with apparatus of the weight and dimensions here used, so that a more flexible arrangement is necessary.

The one first tried, which combines the accuracy of the above with the required flexibility, is shown diagrammatically in fig. 1, plate II where d_1 is the graduated tube at the end of the large reservoir (Cf. *b.* fig. 2), d_2 a steel capillary, d_3 another graduated tube, d_4 the glass capillary and d_5 the bulb. After many trials however and even after measurements had been made, we had to abandon this arrangement owing to the impossibilily of cleaning the steel capillary so thoroughly that it should not spoil the mercury meniscus after this had passed through it.

The arrangement finally adopted is that shown in Plate II, fig. 2. The dimensions of the present apparatus were controlled by the size of the steel apparatus available (designed for 500 At). The steel

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cylinder A Plate I has a length of about one meter and a capacity of about one liter. The glass tube b_3 was chosen as large as possible and has a capacity of about 600 cc. This with its graduations b_4 is connected to the various piezometer bulbs and is of the same type as the piezometer for the highest pressure described in Comm. N°. 50, the internal diameter of b_4 being about 3 mm. The graduations were only made on 20 cm. in order to keep the apparatus within manageable dimensions. The tube b_4 terminates in a capillary tube b_5 of sufficient internal diameter to admit a steel capillary.

The various piezometers, which are all of the same type as that shown in fig. 2 f and fig. 3, are of dimensions corresponding to the various temperatures to be employed so that the pressure which will cause the mercury to appear at the middle of the graduations of the tube b_4 shall be within the prescribed region. The stems f_2 are fine glass capillaries some 70 cm. long to enable them to project above the cryostate Comm. N°. 51, and with internal volumes of about 50 mm.^{3} in order that the temperature correction may be reduced to a small order without at the same time offering too great a retardation to complete equalisation of pressure. At the end of the capillary stem f_2 of the piezometer fig. 4 a small cavity f_3 is made to receive the end of the steel capillary. This cavity must be large enough to avoid any chance contact between the glass and steel and yet not large enough to introduce uncertainties in the volume. It was found most satisfactory to open out the capillary tube in the blow pipe to a diameter and depth of some 1.5 mm. and then to bore the first mm. cylindrical at the lathe. The upper surfaces of both b and f are ground off at right angles to produce a more constant and perfect joint.

The connecting steel capillary g fig. 2 must be long enough to allow of the manipulation of the piezometer without incurring the danger of bending the capillary sharply at any point, a proceeding which usually results in a leak. Under some circumstances a capillary of 40 cm. length could be used, but for the majority of the measurements it was found most convenient to employ one of 130 cm. The capillary is furnished at its ends with screw-connections g_1, g_2 (see fig. 2) to enable it to be fastened securely to b and f.

The various parts can now be readily removed for cleaning, filling etc. while the arrangement is such that it allows the parts to be replaced without producing any appreciable change in the volume up to the graduations on the tube.

The steel tube f_4 with hexagonal portion f_5 and thread f_6 is made about $\frac{1}{10}$ mm. larger than f_2 and is fastened to it by red sealing wax.

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Between the steel flanged tube g_4 and the glass f_2 fig. 4 a washer g_5 of prepared leather is introduced; as however leather gives somewhat under compression it has been found necessary to employ washers which have been subjected for some time to considerable pressure. When the requisite precautions are taken, a joint is obtained which is perfectly tight at 60 Æ and which only requires screwing up one half turn (about 7 mm.) during a long period under this pressure, thus insuring a practically constant volume.

Connections of the type described in Comm. N°. 60, fig. 5, appeared not to allow of sufficient accuracy in the determination of the volume, when the joints were made to stand the pressure in our experiments. Moreover in that case the connection of different piezometer-bulbs to the same graduated tube presents much greater difficulties.

At the lower end of the U tube b_2 fig. 2 of which the leg connected to b_3 is calibrated, the short capillary tube b, carrying a ground joint has been made parallel to the whole length and not bent at an angle as in fig. 4 Comm. No. 50.

The connection with the gas apparatus is made by the short tube h carrying two ground joints h_1 h_3 and a cock h_2. By means of this the tube b containing the requisite mercury can be easily and quickly brought into a nearly horizontal position, when it is necessary to fill it with gas, and the joints closed by rotating tube h. When the tube is filled h_2 is shut b and h removed together, brought into a vertical position and the cock again opened; the mercury then runs quietly into place and tube h can be removed. By this contrivance the troublesome process of turning about the tap h, described in Comm. No. 50 § 1, is no longer necessary.

§ 4. *The compression cylinders, reservoirs and connections.* Like the apparatus described in Comm. N°. 50, the compression cylinder is filled with pure mercury only to which the pressure is transferred also by mercury from the reservoir where it is produced by means of compressed air. Owing to the large volume of mercury required for the tube b the reservoir C must have a capacity of nearly a liter, the level of the mercury in it being indicated by the level tube C_3. A scale C_4 is attached to this tube and the position of the mercury is read by the eye. The distance between the zeros of this scale and that on b_4 is determined by the cathetometer.

The steel head b_6 must be put onto the glass tube b_4 with the precautions mentioned in Comm. N°. 50 especially as the clearance is only some 2 mm. at the bottom of the tube b. On to this head

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b_6 is screwed a water bath b_7 b_8 through which flows a constant upward stream of water of constant temperature. [1])

The steel nut a_3 Plate I and fig. 6, Plate II is divided into two portions connected by screws to enable it to be applied more conveniently. At every joint of this apparatus there is a prepared leather washer between two flat steel surfaces provided with concentric depressions and a central tube. In consequence of the two large washers at a_2 and c_2 being in contact with mercury it has been possible to entirely eliminate leakage at the pressures employed.

§ 5. *The manometer.* The glass portion of this apparatus, made especially for this research, differs little from those employed by VERSCHAFFELT and HARTMAN and could be replaced if necessary by one reading to higher pressures used by the former. The cylinders, reservoir and level tube are identical in construction with those described above for the piezometer only of smaller dimensions. These were so chosen that pressures from 20 to 70 Æ could be read with an accuracy of $\frac{1}{2000}$. Such an accuracy is however only actually obtained by careful preliminary calibrations to determine the volumes of the bulb etc. and the inequalities of the stem, combined with comparisons with the standard manometer at many points over the entire scale.

No attempt was made to determine the normal volume (cf. Comm. N°. 44 note 1) as several measurements of the pressure at the zero of the scale by the standard manometer give an accuracy to this point of some $\frac{1}{200}$ Æ. The capillary depression in the manometer capillary is 7 mm. when the height of the meniscus is 0.1 mm. and in the level tube about 1.5 mm. with a meniscus of 1 mm. The difference must be considered, but is small enough to allow us to assume a constant value the small differences from this being considered as accidental errors.

If we assume that 0.2 mm. can be read with certainty by the eye, and this is probably an underestimate if a mirror is employed, the reading error in the middle of the scale is some $\frac{1}{125}$ Æ, though it is not probable that the comparisons and calibrations can be quite trusted to this high degree.

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[1]) The constancy of the temperatures will be discussed in a later communication.

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The manometer is filled with pure dry hydrogen and is read at temperatures between 15° and 20° C.

In a further communication more details will be given with the measurements, it is sufficient to mention here that the higher pressures deduced from the lowest pressure and determined directly agree very satisfactorily, which we believe is an advance on former apparatus.

§ 6. *Errors belonging to the construction.* In conclusion we may consider the accuracy which we may reasonably expect from such apparatus as that described in § 3.

The volumes of the various portions have been determined to less than

2 mm.^{3} in the piezometer bulbs, 1 mm.^{3} in the piezometer stem, 1 mm.^{3} on the total volume of v_4 (6.0 cc) and certainly less than 3 mm.^{3} from point to point.

The principal cause of error will undoubtedly be the steel capillary with its connections for among many measurements a difference of 1 mm.^{3} was found in the longest capillary with a volume of about 1 cc., we will however assume the error 3 mm.^{3} as reckoned in Comm. 60 § 20.

The cathetometer used to observe the meniscus reads with care to $\frac{1}{50}$ mm. so that an error of $\frac{1}{25}$ mm. may occur in reading the position of the meniscus in v_4 corresponding to a volume of 1.2 mm^3.

The volume of a meniscus of the average height of 1 mm. in a tube of 30 mm.^{2} cross section Ω 10 mm.^{3} with an error at a maximum of 5 %[1]) = 0.5 mm^3.

Hence the total error in the position of the meniscus may be evaluated at $1.2 + 0.5 = 1.7$ mm.^{3} The most unfavorable case gives for the total error $2 + 1 + 3 + 3 + 2 = 11$ mm.^{3} and if we put the probable error 5 mm.^{3}, it appears that the arrangement of the apparatus allows us to reach an accuracy of $\frac{1}{1000}$ with piezometer bulbs larger than 5 cc.

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[1]) SCHALKWIJK, Comm. No. 67.

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Physics. — Prof. H. KAMERLINGH ONNES: "*On* DE HEEN's *experiments about the critical state.*" (Communication N°. 68 from the physical laboratory at Leiden).

§ 1. *Purpose of this communication.* Experiments have been repeatedly described which were alleged to disprove the notion of the continuity of the liquid and gaseous states according to VAN DER WAALS' theory. They especially were said to deny that a simple substance should have only one critical temperature, one critical pressure and one critical volume, that it should possess at a given pressure and temperature above the critical temperature one density only; and that below the critical temperature it can present stable co-existing phases in equilibrium for each temperature only at two definite densities.

Each time however it was possible to point out circumstances which had been overlooked in the experiments. If the experiments mentioned were repeated with due regard to the necessary precautions, they proved to confirm VAN DER WAALS' views.

It required much care to find out the circumstances to which we must attribute the deviations observed in GALITZINE's experiments. At the Leiden laboratory where VAN DER WAALS' theory was made the starting point of several investigations, KUENEN has undertaken this difficult and lengthy work. He succeeded (Comm. N°. 11 May and June '94) in explaining experimentally the phenomena observed by GALITZINE by the influence of admixtures, impurities which amounted to only a few tenthousandths of the substance, considered pure. By this elaborate research we not only considered GALITZINE's views to be refuted but also ideas so nearly related to them as those of DE HEEN. At least it seemed decided, that henceforth no value might be attached to researches on the critical state with simple substances, unless it was proved that even such small impurities as occurred in GALITZINE's experiments were avoided.

KUENEN's experiments failed however to convince DE HEEN that his objections against VAN DER WAALS' theory were not justifiable; nor did it make him aware of the necessity to bestow as much care on the purifying of the experimental substance as we are wont to do. On the contrary, in 1896 [1]) DE HEEN has published new experiments, made with carbon dioxide, again without stating anything concerning precautions taken for its purification.

According to him these experiments would show:

[1]) Bulletin de l'Institut de physique de l'Université de Liège, deuxième fascicule (Bull. de l'Ac. Roy. de Belgique 3e Sér. t. XXXI, '96).

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that a definite critical density, of which the existence has hitherto been accepted, is an entirely ficticious quantity, that in reality there are two critical densities, 1st. the critical density of the liquid, 0.640 for carbon dioxide; 2nd. the critical density of the gas, 0.298 for carbon dioxide, and that the quantity hitherto measured as critical density is the mean of these two limiting densities.

Shortly afterwards a visit of DE HEEN to Leiden offered an opportunity for a discussion in which I pointed out, that very small deviations in temperature, pressure and composition near the critical state can lead to great variations in density. My remark that in DE HEEN's experiment the carbon dioxide had not been perfectly pure was not contradicted. Whereas to me this circumstance seemed very important, DE HEEN did not set much value upon it.

It seemed that the controversy could be solved by repeating at the Leiden laboratory DE HEEN's measurements in his own apparatus with carbon dioxide of the same purity as it is used with us for similar experiments. During the repetition of these measurements other precautions which seemed desirable to me might also be taken. I found Dr. J. E. VERSCHAFFELT, then assistant at the Leiden Laboratory, willing to undertake the work and Prof. DE HEEN was kind enough to send to Leiden the "analysateur de l'état critique". But when we began working the apparatus, it proved unfit for experiments with very pure carbon dioxide. For the liquefied gas came into contact with the packing. This was made of leather soaked with wax or grease, which substances dissolve in the liquid carbon dioxide so much that they can even be distinctly smelt when the liquid is drawn off. The packing boxes did not allow us to substitute for the leather packing, cork or lead. Even if the carbon dioxide before being admitted into the apparatus had been as pure as we desired it, the results obtained would not have related to pure carbon dioxide. Besides the introduction of new packing boxes, the apparatus called for radical modifications in order to allow us to inquire whether, even though it remained impossible to verify the homogeneity of the phases, the two quantities of the substance, of which DE HEEN in each case compares the densities, have indeed the same temperature and pressure. DE HEEN supposes that this is true, but the construction of the apparatus used by him does not permit of a proof.

Hence we could only profit from the presence of the apparatus at Leiden by studying some of its peculiarities, and the matter was not further entered into.

In '97 DE HEEN thought that he found a proof of the exactness

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of his observations in those of AMAGAT. He derived from AMAGAT's experiments that there are two densities near the critical point, which are in the ratio of 1 : 2 and he wrote: J'ai du reste la conviction que la théorie que je viens de soutenir ne commencera à se généraliser que lorsque les expériences — namely those with the analysateur de l'état critique — auront été répétés un grand nombre de fois par plusieurs physiciens. Ce n'est que dans ces conditions qu'on peut porter atteinte à des convictions — the existence of one critical state — ayant poussé de si profondes racines.

The result of a careful repetition of those experiments could however not be doubtful in our opinion. For who ever wishes to repeat DE HEEN's measurements of density, will want to arrange the work so that it will be possible to verify the homogeneity of each of the phases, and to measure accurately small differences in temperature, pressure and composition of the phases to be compared, in order to calculate by them corresponding corrections. It would also be desirable to apply even now similar corrections to the numbers given by DE HEEN, in order to arrive thereby at the true results of his researches. But as DE HEEN has paid no attention to the data for the determination of these corrections, this is not possible. We nevertheless can form an idea of their general character. And so Dr. VERSCHAFFELT and I in going over DE HEEN's experiments were soon convinced that these, however improbable this may seem to him, would agree with VAN DER WAALS' theory within the limits of the errors of observation after the necessary corrections had been applied.

In order to show moreover experimentally that such corrections must be actually applied an apparatus — chiefly consisting of two reservoirs connected by a cock, from each of which the contents could be collected by a small cock — was constructed of several pieces available in the laboratory, with which we intended to repeat some of DE HEEN's measurements with the necessary precautions.

When Dr. VERSCHAFFELT left Leiden, I have myself devoted some time to preliminary observations with an improved apparatus better answering the purpose. Among other things I had introduced a thermo-element in each of the reservoirs mentioned.

During these preliminary measurements nothing was observed (see following sections) that could point to the important deviations which were derived by DE HEEN from the experiments chosen for repetition, and it was confirmed that it was necessary to apply corrections to the densities given by him.

Hence a continuation of this repetition of DE HEEN's experiments

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appeared to be only useful in that it exhibited by means of his results the amount of deviation which can be found, whenever we are not guided by the theory of the mixtures and of the adiabatic variations of state in measurements with compressed gases in the neighbourhood of the critical state. The most important point in this question, namely the influence of small admixtures on the phenomena in the neighbourhood of the critical state, will be illustrated by other investigations which are being made here and as I hope even better than could be done by the measurements mentioned.

More urgent work obliged us to leave undone the measurements in which the conditions for the deviations given by DE HEEN were intentionally realized, and the apparatus was taken to pieces. Nor did my time allow me to make further investigations in connection with DE HEEN's experiments. In the "Mathemathische Encyclopædie" I hope to return to some questions relative to the theory of the critical state. And what could be remarked on DE HEEN's experiments, seemed to me after I had tried to write down something on them not sufficiently interesting for a paper.

But a few days before the last meeting I received DE HEEN's paper „les légendes du point critique", in which he expresses in a friendly tone his earnest wish that I should now communicate publicly my opinion on his work.

I avail myself of this opportunity to express to Prof. DE HEEN in return my feelings of friendship and respect. I have tried to satisfy his request by what I have said above and by explaining it more in detail in the following sections.

2. *Investigation of one of the systematic deviations.* KUENEN has already pointed out how unsatisfactory is a refutation of theories so little defined as those of DE HEEN. The refutation of the results derived by DE HEEN from his measurements by repeating them is as little inviting. Since it is a repetition we are bound to a method of working deviating much from that, which we should think it necessary to follow in similar investigations. Moreover what we call taking precautions may be considered by DE HEEN as sacrificing an artifice, lastly to attain a moderate accuracy in measurements with compressed gases, operations are necessary which require much time and care. If therefore in the repetition of DE HEEN's experiments a high degree of accuracy was required I would not have undertaken it. But a determination of density to within 3 percent is sufficient, as the deviations between DE HEEN's results and those which

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can be derived from the laws generally accepted, even at several degrees' distance from the critical temperature, amounted in some cases to 30 and 40 percent [1]). Also for the experiments to be considered below, the deviation is large enough to be refuted by measurements of the accuracy mentioned. Besides it is a favourable circumstance that all the deviations are connected systematically. It is easy to see this from DE HEEN's table. (l. c. p. 386). If therefore one of the important deviations mentioned by DE HEEN can, by the repetition of the experiment from which it was derived, be reduced to zero within the limits of the errors of observations, this involves the refutation of all the others.

Although I will not dwell on the theoretical considerations refuted by KUENEN I must shortly explain which is the chief point in the experiment to be repeated.

DE HEEN assumes the existence of so-called liquidogen and gasogen molecules. The former would only be decomposed far above the critical temperature. If we succeed in filling a space near or just above the critical temperature entirely with liquidogen molecules then the substance enclosed therin will have one of the limiting densities given by DE HEEN for the critical state; if we succeed in doing the same for the gasogen molecules, the second limiting density will be observed. Above the critical temperature, mixtures of those kinds of molecules can be made in all proportions. If a space filled with liquidogen molecules is in contact with an other containing gasogen molecules, so that mutual diffusion can take place, the liquidogen and the gasogen molecules will be mixed. Only when they have been completely mixed — and so after some time — the difference between the densities in these two spaces disappears.

DE HEEN's analysateur de l'état critique renders it possible by means of a cock to divide the volume occupied by a substance into two parts at a moment of pressure equilibrium and in this way if one space contains chiefly liquidogen, and the other chiefly gasogen molecules, to prevent the mixing of these two. The substances in each of the two reservoirs mentioned in § 1, which are placed above each other and are separated by a cock, can moreover be separately collected by means of cocks made for this purpose. According to DE HEEN it would be possible by taking care that at first the lower reservoir should be filled chiefly with liquid, and the upper reservoir chiefly with vapour, to fill above the criti-

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[1]) For instance, influences like those of gravitation (Comp. Comm. N°. 17 KUENEN, May '95,) can be left out of account.

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cal temperature one space chiefly with liquidogen, to other chiefly with gasogen molecules under the same pressure. At the same pressure and the same temperature different densities would then be found in the two spaces.

DE HEEN has not made clear, what could be learned better from the experiments with the "analysateur" than from the experiments with the tubes of GALITZINE.

For in the latter case the two phases, the one consisting chiefly of supposed liquidogen molecules, the other chiefly of supposed gasogen molecules, are heated separately, while the movable mercury thread which separates them is constantly yielding to the difference of pressure between the two phases, and indicates if the equilibrium is not attained, for which difference of pressure a correction is to be applied in the comparison of the densities.

As compared with this contrivance the making of a partition between the space where more liquidogen, and that where more gasogen molecules are supposed to be, by means of a cock which is only opened now and then, may be considered as a step backwards. In this way mixture by means of diffusion cannot be avoided so well, nor can the equilibrium of temperature and pressure be so well attained or accounted for. If DE HEEN had succeeded in separating perceptibly the liquidogen and the gasogen molecules, then they ought to have been observable certainly in GALITZINE's tubes, as indeed this physicist thought. KUENEN by his experiments has proved that this was not the case.

If discussion of DE HEEN's theses was primarily required then we might argue that everything derived by DE HEEN from the experiments with the "analysateur" has been à fortiori refuted by KUENEN's criticism of GALITZINE's arguments.

But our aim was to demonstrate by the repetition of DE HEEN's experiments with the necessary precautions, that they lead to other results than those given by DE HEEN. Like DE HEEN we used for this purpose two metal reservoirs separated by a cock.

I must still mention one point of difference between the „analysateur" and our aparatus meant in § 1. The reservoirs of our apparatus have an invariable volume. This is not the case with the „analysateur". In each of the cylindrical reservoirs of the "analysateur" a piston can be moved and these two pistons are so connected, that when they are moved the volume occupied by the substance in the two reservoirs together remains unaltered. By adjusting the pistons properly and by filling only one of the reservoirs, any suitable quantity of liquid can be admitted into the

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apparatus, which may be distributed by means of the connecting cock over the total space of the two reservoirs, after which by re-adjusting the pistons the total space can be again divided into two parts of a desired ratio by means of the cock. And so it is easy to make a series of different measurements for different ratios with the same apparatus. It is also possible to alter the proportion of the two volumes during an experiment. It is obvious that the first mentioned speciality is useless in the repetition of a given experiment, it being moreover of little importance, as the desired filling can also be made in an other way, for instance by distillation, and as DE HEEN uses for the first series of experiments only one proportion and for the other only two extreme proportions. As will be seen, what might be attained by moving the piston during the experiment, is from DE HEEN's reasoning of no importance for the results to be obtained by repeating his experiment, or may be arrived at in another way.

After this digression we come to consider the experiment of DE HEEN which I had chosen for repetition. In this (Bulletin de l' Institut de Liège Deuxième fascicule p. 150) the pistons of the analysateur are placed so that the volumes of the two reservoirs are equal. Then the two reservoirs are filled at 10° C. with liquid carbon dioxide and the connecting cock is closed. The carbon dioxide from the upper reservoir is blown off, the connecting cock is opened, the carbon dioxide is allowed to fill the two reservoirs and to reach equilibrium, and then the apparatus is heated to 35° C. After the connecting cock is closed the contents of the two reservoirs are separately collected. For the density at 35° C. in the upper cylinder DE HEEN gives 0.456, for that in the lower cylinder 0.544, whereas according to VAN DER WAALS the densities of two quantities of pure carbon-dioxide, no matter how they are obtained, must be the same under the same pressure at 35° C.

The reason why this special experiment has been chosen for repetition is that it lies not too near the critical temperature and yet shows important deviations; also because according to AMAGAT's data the surface of the liquid in the apparatus at 28° C. stands very near the cock; and lastly and chiefly because in this case DE HEEN does not move the pistons of the "analysateur". For this reason it could be repeated with the apparatus described above, as the latter has two metal reservoirs of unvariable and almost equal volume with a connecting cock. And so the apparatus is for this experiment equivalent to that of DE HEEN.

Carbon dioxide was admitted into it which had been distilled at ordinary temperature over phosphorus pentoxide and boiled at a low temperature, and which in the liquid state had been into contact

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with clean metal only. Before the carbon dioxide was admitted, the apparatus had been evacuated by a BESSEL HAGEN's airpump. Auxiliary apparatus of which the volume had been measured, rendered it possible to admit by distillation the exact weight of carbon dioxide into the two reservoirs with open connecting cock. Care was taken that the liquid carbon dioxide was exclusively contained in the lower reservoir. During the heating namely, the temperature of the upper reservoir was kept a little above that of the lower reservoir, so that below the critical temperature no liquid could distil over from the lower reservoir into the upper reservoir. It seems to me that in this way better than by the method of the moving pistons, as followed by DE HEEN in his later experiments, certainty may be obtained that at the beginning as little liquid as possible is found in the upper reservoir.

The connecting cock was closed at 28° C., then the temperature was raised to 35° C. by streaming water of this temperature. During the heating the cock was opened six times for 4 secunds, and after the heating another 6 times for 4 secunds at constant temperature. Several experiments had proved, that 4 secunds was a time long enough to secure equilibrium of pressure. In this time equilibrium of temperature was not yet attained, but it was not necessary with my apparatus to wait for it, as the temperature could be determined by the thermo-element in the two reservoirs separately, and so a correction could be applied. In DE HEEN's reasoning the liquidogen and the gasogen molecules in my experiment must have had less opportunity of escaping observation by their diffusion, than with his own experiment, where the cock was left open while heating from 28° C. to 35° C. When the cock was closed at 34.°8 C. the ratio of the densities was $\frac{0.448}{0.426} = 1.052$. By applying the correction for the difference of temperature 0.8 deg. as given by the thermo-elements (the real difference was probably smaller) this ratio would become $\frac{0.448}{0.467} = 0.96$. For permanent gas no correction was required as it amounted in the analysis of the original gas-phase to 0.00018 only and in that of the original liquid-phase to 0.00016 only.

And so only a small deviation was found becoming opposite in sign to that of DE HEEN by a correction of uncertain amount, which result, taking into account the errors of observation, would be expressed in DE HEEN's language by the statement that the liquidogen and the gasogen molecules are the same.

A second experiment must be mentioned in which the connecting

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cock was left open during the heating from 28°C. to 35°C., heat being applied from above, and where I allowed 10 minutes for the attainment of equilibrium in the temperature and pressure. This period is probably too long to allow us to consider this experiment as a repetition of DE HEEN's, but certainly not sufficient for the two kinds of molecules to get mixed in a considerable degree through the narrow cock by diffusion according to our ordinary views. When the cock was closed at 35°.4 C. the ratio of the densities was $\frac{0.448}{0\,432} = 1.037$. By applying the correction for the difference of temperature of 1°.15C. as given by the thermo-elements, this proportion would become $\frac{0.448}{0.492}$ and by correction for the permanent gas, found at the analysis to be 0.002, $\frac{0.449}{0.494} = 0.91$.

Although as said in § 1 I attach no other importance to these numbers than that of preliminary observations, yet they are sufficient to regard DE HEEN's measurement, which gave the ratio $\frac{0.544}{0.456} = 1.19$, as disproved (especially by the first experiment).

Even if I suppose the error of observation in my densities to exceed 3 pCt., then DE HEEN's much larger deviation still remains disproved.

Nor can my proof be weakened by the fact that the differences of temperature were certainly over-estimated, and that with other less complete measurements of the same series which, as I have said already, were treated entirely as preliminary observations, deviations of the uncorrected densities were found which amounted even to more percents and which were in the sense of DE HEEN; on the contrary they showed, I think, that the errors which are likely to be made, tend towards the direction of the deviations found by DE HEEN.

And so DE HEEN's statement "ainsi se trouve mis hors de doute cette proposition tant contestée que nous avons émise depuis longtemps: La température et la pression ne suffissent pas toujours pour définir la densité d'un fluide" — is not in the least supported by his experiments.

§ 3. *Explanation of the deviations found above the critical temperature.* It is certainly remarkable that the differences given by DE HEEN which we have shown to be due to the neglection of corrections, are so considerable.

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There is no objection for supposing that differences in temperature have remained e.g. in consequence of compression in the one reservoir and expansion in the other, which necessarily attend the transport of substance from the lower into the upper reservoir, which moreover was very likely also warmer for other reasons.

I would be inclined however to ascribe the deviations for a part to the presence of impurities. The carbon dioxide obtained from commercial cylinders, contains sometimes a few percents of its volume of admixed air, besides traces of water vapour. DE HEEN has compressed it by means of a compression-pump, and it is known how difficult it is to keep a gas pure during this operation. Moreover it appeared necessary in DE HEEN's experiments in order to condense the carbon dioxide at 10° C in the apparatus to raise the pressure to 75 atmospheres, whereas the saturation pressure of carbon dioxide at that temperature amounts to only 45 atmospheres.

We have seen that the liquid carbon dioxide dissolves the wax and grease of the packing. In the gaseous phase the molecular pressure will decrease by the admixture of more volatile substances, and in the liquid phase it will be increased by the less volatile admixtures. Owing to the large compressibility in the neighbourhood of the critical state, the densities belonging to a same external pressure may show considerable differences.

If the two phases of different composition are raised to a higher temperature the influence of the deviation in the molecular pressure will be diminished. And so the differences of density will be smaller. This is also the result obtained by DE HEEN.

In order to avoid as much as possible the diffusion of the liquidogen and gasogen molecules during the long time which is required to attain the equilibrium at a higher temperature, DE HEEN makes these experiments in the following way:

„il suffit de porter l'appareil à une température peu supérieure à la température critique, par exemple 35°, puis de fermer la clef *D* (the connecting cock) tout en continuant à chauffer jusqu'au point voulu. Lorsque celui-ci est réalisé on ouvre *D*, on laisse l'équilibre s'établir. Puis on recueille séparément l'acide renfermé dans les deux cylindres."

From this it may be seen that the artifice of which we availed ourselves in heating to 35° C. has been borrowed from DE HEEN.

From the system of isothermals (pressure, volume) may be seen at a glance that the pressure for the two phases with densities on either side of the critical density will increase very differently by heating at constant volume, so that when the desired temperature

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is attained, a considerable difference of pressure will exist between the two phases before the cock is opened. This causes on opening the cock a difference of temperature, which would prevent the equalization of densities from being completed when the process was purely adiabatic. With the slow transport of heat, which in reality takes place, equalization will be still retarded.

Before DE HEEN could therefore set any value upon the densities found after the closure of the cock, as belonging to a same temperature and pressure, he ought to have shown that the equilibrium of temperature had been obtained. With my apparatus treated in § 2 the process might be interrupted at any time, as soon as the equilibrium of pressure had once been attained, because the remaining difference of temperature could be determined and accounted for. But this was not so in the case of DE HEEN.

It is obvious that as the cock is left open during a shorter time, a greater difference of temperature will remain. The corrections to be applied will accordingly be the greater. In a series of observations, if the cock is opened in the same way every time, they will follow a systematic course, like the corrections for the small admixtures, if the carbon dioxide used was always of the same composition, and like any other correction, which belongs to an operation always performed in the same way e.g. the manner of heating.

Obviously larger corrections must be applied to DE HEEN's second series of experiments, which he performed in order to avoid diffusion, in the following way:

"Il faut donc amener les pistons dans la position (fig. 6) ou (fig. 7) — giving a definite ratio between the volumes of the reservoirs — à une température un peu inférieure au point critique, puis on ferme *D* et on continue à chauffer jusqu' à une température voulue. Pendant que la température s'élève on ouvre de temps en temps et rapidement[1]) le robinet *D*, de manière à permettre à la pression de s'équilibrer dans les deux cylindres, tout en empêchant les molécules liquidogéniques du cylindre inférieur de se diffuser dans le cylindre supérieur." —

Whereas in the experiment discussed in § 2 DE HEEN arrived at the two densities 0.456 and 0.544 or the ratio 1.19, he gives as results in the second series under almost the same circumstances the densities 0.360 and 0.550 and so a ratio of 1.44, where I found the theoretical ratio 1.00 sufficiently verified. And so in my

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[1]) About 5 times, lasting 4 seconds each, as DE HEEN was kind enough to inform me.

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opinion an extraordinary large correction must be applied for systematic errors.

Part of the systematic errors must be due to the shortness of the time during which the cock is opened. Near the critical state it is indeed an inefficient means for obtaining the desired equilibrium of pressure and temperature.

DE HEEN has been aware that when the cock was opened once only, a difference in temperature could arise by the expansion of the substance in the lower reservoir. But it seems to have escaped his notice, that in the very neighbourhood of the critical state the adiabatic process is not at all favourable to equalization of pressure.

The process can be traced graphically by means of a diagram of the isothermals and adiabatics near the critical point.

It will be sufficient to show its character. Hence it will be allowable to simplify it and to trace the variations of two equal masses of the two phases, which are heated both at a constant volume, then are adiabatically brought to equilibrium of pressure, then again heated isometrically to a higher temperature, once more brought to equilibrium of pressure adiabatically etc. We then neglect the modification undergone by each of the phases owing to the exchange of substance which takes place from the one reservoir into the other.

In order to arrive at a definite diagram of the adiabatics and the isothermals, we may for simplicity imagine it as derived from VAN DER WAALS' equation of state. Near the critical point the adiabatics coincide almost with the lines of constant volume, and so adiabatic equalization of the difference of pressure will hardly give a variation of the specific volume. The phases which first at equal temperatures differed in pressure, after equalization of pressure differ so much in temperature, that the density is only slightly changed. The difference of pressure has been transformed into a difference of temperature almost equivalent with regard to the difference of density, and this difference of temperature with a slow transport of heat will in reality not vanish when the cock is closed after a few seconds.

When the cock is opened for a short time this should be repeated very often in order to ensure the equilibrium of temperature.

This reasoning was confirmed by my observations with the thermo-elements. After having heated the apparatus from 28° C. with closed cock to 35° C. and opening the cock according to DE HEEN'S method only 5 times for 4 seconds, I repeatedly found after successive further openings of the cock a renewed difference of temperature.

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The observations have not been made accurately enough to set much value upon the numbers obtained, but they always tended to show a heating of the upper reservoir by the opening of the cock. (On an average 0°.27 C. in the experiment of § 2).

Besides the difference in the treatment of the cock, DE HEEN's second series of experiments is distinguished from the first by a second modification, which favours greater differences. Let us here consider only DE HEEN's two experiments mentioned above. In both cases the apparatus is heated from 10° C. to 35° C. and it contains a quantity of substance, which when distributed over the whole space, would show almost the critical density (according to current views). In both cases the apparatus is filled by first adjusting the pistons so that the total volume is exactly divided into two parts, and by then filling the one reservoir completely with liquid at 10° C. and distributing this quantity of substance over the two reservoirs.

But in the first series the apparatus is then heated without further operations. In the second series by readjusting the pistons all the substance is first brought below the cock, the apparatus is heated to a little below the critical temperature and then the piston is adjusted until a definite ratio between the space of the lower reservoir and of the upper reservoir is obtained. That ratio is $\frac{0.155}{0.845}$ when a determination of the density of liquid is wanted, $\frac{0.771}{0.229}$ when a determination of the density of vapour is wanted. And so the surface of the liquid is shifted in the apparatus while the ratio of the phases remains constant.

I may here mention that for this operation I constructed the compound hydraulic pump, which VAN ELDIK has used for his measurements on the capillarity of mixtures (Fig. III. Communication N° 39 May '97). This apparatus seems to me preferable to the "analysateur" because the phases can be observed in a glass tube and need not come into contact with the packings but only with mercury and glass.

The influence of the packing on the observations with the "analysateur" has been mentioned previously. We have now to consider the influence of the operation mentioned on the result of the experiments.

The experiments, in so far as they deal with a temperature below the critical, will be considered sub. 5, it will here be sufficient to say that the experiments above the critical temperature have to decide whether the substance, originally in the liquid state (at an almost constant volume) will have a higher density when raised above the

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critical temperature than the substance which originally was in the gaseous state and assumes the same temperature and pressure. The movability of the pistons is of no consideration for the experiments above the critical temperature, the only important thing is that below the critical temperature the same distribution is obtained which DE HEEN had realized at the moment when the pistons are brought into their last position. One of the ways in which I obtained that distribution in an apparatus with two reservoirs of the ratio given by DE HEEN in his second series was distillation.

Probably in choosing the ratio mentioned, DE HEEN expects to be able to separate from the gas above and from the liquid below a phase more exclusively consisting of liquidogen or gasogen molecules than when the reservoirs have the same volume. The substance chiefly consisting of gasogen molecules is related according to him to that chiefly consisting of liquidogen molecules as a dilute solution of salt is to one more concentrated on which it floats. If the two have during some time been in contact the nearest approach to the original concentration of the two solutions of salt will be obtained by drawing off at one end the upper layers, at the other end the lower layers. In this reasoning we may put in the place of DE HEEN's hypothetical liquidogen molecules the really existing very small admixtures to the carbon dioxide. In the initially wholly or chiefly liquid portion of the carbon dioxide they amount to another number than in the initially wholly or chiefly gaseous portion and only gradually they will be distributed equally by diffusion. According to § 2 it is obvious that greater corrections must be applied to the observed densities when the substance of which the density is measured is taken from the extreme layers than when they are taken from the intermediate layers. And so a more unequal distribution of the admixtures over the two reservoirs may also have attributed to the larger differences given by DE HEEN in his second series.

At any rate, now that DE HEEN's first series of which the deviations are systematically related to those of the second, has been refuted, his measurements of the second series do not in the least prove his theses:

"Il est aisé de conclure de ce résultat que la densité critique qui a été admise jusqu'à présent est une densité purement fictive (and further what has been cited in § 1). 3° la loi du diamètre est parfaitement observée, ainsi que la planche l'indique. Si l'on prolonge celui-ci jusqu'à la température critique, on obtient la densité critique *fictive* qui avait été admise jusqu'à présent, 0.470. 4° Les courbes exprimant les variations de densité du liquide et

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de la vapeur se prolongent au dessus de la température critique, et ce n'est que vers 60°, en général que la masse devient homogène dans toutes les parties du tube (en employant toutefois les précautions indiquées)."

4. *Explanation of the deviations below the critical temperature.* DE HEEN's statement that for carbon dioxide in the case of the co-existence of liquid and vapour as far as about 20 deg. below the critical temperature no definite densities would exist for the vapour and the liquid, but that for instance at 28° C. this density would be situated for vapour between the limiting values 0.288 and 0.533, for liquid 0.408 and 0.650, disagrees in my opinion with the experience of all who have made accurate measurements with liquefied gases.

And though in repeating DE HEEN's determinations with the above-mentioned apparatus I have found small deviations from the liquid and vapour densities found by AMAGAT, they could always be attributed to errors of observation.

This statement of DE HEEN may be explained by the fact that the meniscus cannot be seen in the "analysateur." And so DE HEEN may have given as density of the vapour phase the mean density of matter in a reservoir in which the meniscus had risen already, and as density of the liquid phase the mean density of matter in a reservoir in which the liquid surface had fallen already.

Dr. VERSCHAFFELT has combined in a very clear diagram DE HEEN's data by plotting the densities given by the latter for the vapour phase and those given for the liquid as ordinates, and the mean density of matter in the two reservoirs of DE HEEN as abscissa. For simplicity I borrow from that diagram only a small number of lines (see fig. 1 p. 643) and give by its side in fig. 2 those which indicate the mean densities mentioned, in each of the reservoirs according to AMAGAT's vapour and liquid densities (the line applying at the critical temperature and higher, has been drawn at an angle of 45°).

It is obvious from these figures that DE HEEN in the calculation of his densities has neglected the correction from non-homogeneous to homogeneous substance. By applying this correction his observations would give a vapour and liquid density almost independent from the mean density of matter, which by means of corrections systematically related to those considered in §§ 2 and 3, would very likely be made to agree with those of AMAGAT within the limits of the errors of observation.

Everything being considered it appears desirable that DE HEEN should

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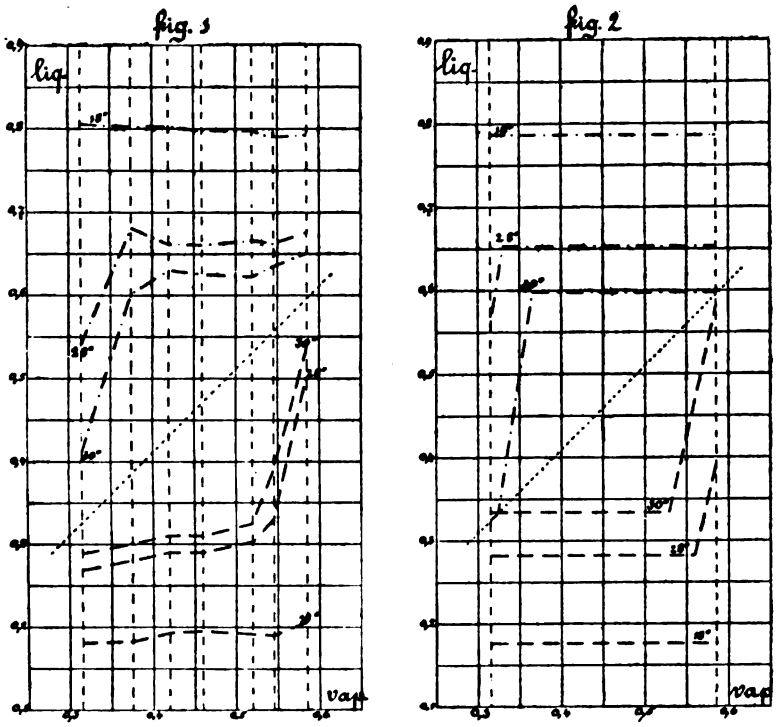

repeat his experiments with due regard to the circumstances and the corrections indicated in this paper.

I think I have sufficiently justified the opinion that these experiments bring no arguments against the truth and the completeness of the theses from VAN DER WAALS' theory on the critical state mentioned at the beginning of § 1.

Physics. — Prof. VAN DER WAALS on: "*The equation of state and the theory of cyclic motion*". III. (Continued from p. 584).

There is another quantity relating to the critical point, which calculated from the equation:

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT, \quad \ldots\ldots\ldots \quad (1)$$

if b is kept constant, yields a value strongly deviating from what is found for it by means of the experiment. The quantity $\left(\frac{T}{p}\frac{dp}{dT}\right)$, calculated for the tension of saturated vapour, coincides in the critical

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point with $\left(\frac{T}{p}\frac{dp}{dT}\right)_v$. The experiment shows that for many substances its value does not differ much from 7, whereas from the equation of state, if b remains constant, we find no more than 4.

If we write:

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_k = \frac{T}{p}\left(\frac{dp}{dT}\right)_v = \left\{1 + \frac{1}{p}\left(\frac{d\varepsilon}{dv}\right)_T\right\}_k,$$

it appears that this value is quite determined by the properties of the substance at the critical temperature; but that it is not determined by the course of the critical isothermal alone. Not from every equation, which perfectly represents the course of this isothermal, a correct value will be found for it. In so far it differs from $\left(\frac{pv}{RT}\right)_k$, which is quite determined by the isothermal, and for which therefore the true value may be found from every equation which represents the isothermal. Only for such an equation which besides representing correctly the isothermal, also assumes the accurate value for ε and so also for $\left(\frac{d\varepsilon}{dv}\right)_T$, the true value for $\left(\frac{T}{p}\frac{dp}{dT}\right)_k$ can be found.

It is known that if in the equation (1) b is kept constant, and if we take a as depending on the temperature, the factor 4 rises to 7, if we assume such a dependance on the temperature, that:

$$-\frac{T}{a}\frac{da}{dT} = +1$$

at $T = T_k$. It will appear from what follows, that the compressibility of the molecule, or to use a safer term the variability of b, will raise the value of $\left(\frac{T}{p}\frac{dp}{dT}\right)_k$ to nearly 7, even without a being a function of the temperature.

Let us write again:

$$\varepsilon = f(T) + P_v - T\left(\frac{dP_v}{dT}\right)_v + P_b - T\left(\frac{dP_b}{dT}\right)_b$$

then we find:

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_k = 1 + \frac{1}{p_k}\left\{\frac{dP_v}{dv_T} - T\frac{d^2P_v}{dv\,dT} + \frac{db}{dv_T}\left[\frac{dP_b}{db_T} - T\frac{d^2P_b}{db\,dT}\right]\right\}_k.$$

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If we restrict ourselves to the term $\frac{dP_v}{dv_T}$, so if we do not assume the quantity a in the expression $\frac{a}{v^2}$ to be a function of the temperature, then:

$$\left(\frac{T}{p}\frac{dp}{dT}\right) = 1 + \left(\frac{a}{pv^2}\right)_k.$$

On the supposition that b is constant, p_k has the value of $\frac{1}{27}\frac{a}{b^2}$ and v_k the value $3b$ and we calculate $\left(\frac{T}{p}\frac{dp}{dT}\right)_k = 1 + 3 = 4$.

If however, b is variable and if this quantity follows a course as discussed in the preceding pages, then $p_k = \frac{7}{6} \cdot \frac{1}{27}\frac{a}{b_k^2}$ and $v_k = 2{,}03\ b_k$, and we find:

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_k = 1 + 5.7 = 6{,}7,$$

in perfect accordance with what I had previously calculated for it, viz. $\frac{2{,}9}{0{,}4343}$. (Continuiteit I p. 159). Also to this quantity applies what has been observed for $\left(\frac{pv}{RT}\right)_k$, viz. that if a reason is found which reduces the critical volume from 3 to about 2, the other quantities characterizing the critical point, which differ much from the previously calculated values, are at the same time corrected.

But then it appears at the same time that:

$$\left\{\frac{1}{p_k}\frac{db}{dv_T}\left[\frac{dP_b}{db_T} - T\frac{d^2P_b}{db\,dT}\right]\right\}_k$$

must be equal to 0, or at any rate so small that it may be neglected. Now $\left(\frac{dP_b}{db}\right)_T$ is equal to:

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$$\left(\frac{dP_b}{db}\right)_T = \frac{f\,RT}{(b-b_0)} - \left(p + \frac{a}{v^2}\right)$$

or

$$\left(\frac{dP_b}{db}\right)_T = \left(p + \frac{a}{v^2}\right)\left\{f\,\frac{v-b}{b-b_0} - 1\right\}.$$

If we therefore put:

$$\varepsilon = f(T) - \frac{a}{v} + P_b$$

then:

$$\left(\frac{T\,dp}{dp\,dT}\right)_k = \left(1 + \frac{a}{pv^2}\right)_k \left\{1 + \frac{db}{dv_T}\left(f\,\frac{v-b}{b-b_0} - 1\right)\right\}_k.$$

According to the values which $\frac{db}{dv_T}$ and $\frac{v-b}{b-b_0}$ have in the critical point:

$$\frac{db}{dv_T}\left(f\,\frac{v-b}{b-b_0} - 1\right) \text{ would be } 0{,}138\left(2\,.\,\frac{21}{15} - 1\right)$$

or about 0,248.

From this follows that if $T\,\frac{d^2P_b}{db\,dT}$ was equal to zero, we should have to add nearly $^1/_4$ of 6,7 to the value of $\left(\frac{T\,dp}{p\,dT}\right)_k$ — and consequently this value would not be found too small, but much too large. This error is avoided, if we put:

$$T\,\frac{d^2P_b}{db\,dT} = \frac{dP_b}{db}$$

which is the case, as we observed when calculating the specific heat, if we assume the atomic forces as proportional to the temperature.

The consequences of such an assumption are somewhat strange. In this case $b_g - b_0$ would be the same for all temperatures, and b does not depend on the temperature. Then the molecules are compressible, but do not expand by heat, which is in opposition to what I expected at the beginning of this investigation. And I must confess that in spite of the many remarkable results which we have obtained, and which are acceptable, this result has made me doubt whether the calculated formula for b, though it indicates

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the course of b fairly accurately, has really the theoretical signification, which we should assign to it, if we use it to explain such large changes in the value of b, as is given for it by the equation of state. But we met already with the same difficulty in the determination of the specific heat, for the rotations, which we have to assume, if there is no potential energy for the molecule, are in themselves very probable. That the result is very near the truth seems to appear from what follows. A gas follows the law of BOYLE at very large volumes, as:

$$\frac{a}{RT} - (b_g)_T = 0.$$

If we introduce the critical temperature, which according to what precedes is but little below:

$$RT_k = \frac{8}{27}\frac{a}{b_k}$$

we find:

$$\frac{T}{T_k} = \frac{27}{8}\frac{b_k}{(b_g)_T}.$$

So, if we keep b always constant in the equation of state, the result is that the temperature, at which a gas in the utmost rarefied state follows the law of BOYLE, is $\frac{27}{8}$ times higher than the critical temperature. If on the other hand, we assume b to be variable with the degree of density, and if we bear in mind that b_k amounts to about 0,86 of b_g, as it is at the critical temperature, the preceding equation becomes:

$$\frac{T}{T_k} = \frac{27 \times 0{,}86}{8}\frac{(b_g)_{T_k}}{(b_g)_T} = 2{,}9\frac{(b_g)_{T_k}}{(b_g)_T}.$$

According to a remark of DANIEL BERTHELOT (Quelques remarques etc. Arch. Néerl. Tome V pag. 439) the experiment furnishes the value 2,93 to 2,98 for the proportion of these temperatures. From this value we may most likely conclude that the value of b_g is the same at these two temperatures which differ so widely. If therefore I continue speaking of the compressibility of the molecules, I do so with reserve, but yet in the expectation that this question may be decided

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by further investigation, when some more trustworthy series of values of b at widely differing temperatures will have supplied values for the coefficients of the equation.

If we accept the result, that the temperature has no influence on the value of b, as perfectly correct, then $\left(\frac{Tdp}{pdT}\right)_k$ may be brought under the following form:

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_k = \frac{1}{1 - \frac{3}{4}\frac{1-\alpha}{1-\alpha-\beta}}.$$

Between $\left(\frac{pv}{RT}\right)$ and $\left(\frac{T}{p}\frac{dp}{dT}\right)$ we find the following relation:

$$\left(\frac{pv}{RT}\right)_k \times \left(\frac{T}{p}\frac{dp}{dT}\right)_k = \frac{\frac{3}{2}}{1-\alpha-\beta}.$$

If b is kept constant, then $\left(\frac{pv}{RT}\right)_k = \frac{3}{8}$ and $\left(\frac{T}{p}\frac{dp}{dT}\right) = 4$, and the product furnishes $^3/_2$, the value of the second member if α and β are zero. If $\left(\frac{pv}{RT}\right)_k = \frac{1}{3,4}$ and $\left(\frac{T}{p}\frac{dp}{dT}\right) = 6.7$, as we have calculated for CO_2, we find $1 - \alpha - \beta = 0,762$, quite in accordance with the formerly accepted values of α and β.

So the equation of state of a substance continues to contain two parameters a and b. For a we have assumed that this quantity is constant, but for b that it depends on 3 constants, viz. b_g, b_0 and f.

By means of the given relation between b and the three constants, on which it depends, the three quantities b_k, α and β are determined (we shall presently return to this determination). The experiment furnishes four data, from which inversely the four unknown quantities a, b_k, α and β might be calculated. The four data of the experiment are, v_k, p_k, RT_k and $\left(\frac{T}{p}\frac{dp}{dT}\right)_k$ — for which we can also take p_k, RT_k, $\left(\frac{pv}{RT}\right)_k$ and $\left(\frac{T}{p}\frac{dp}{dT}\right)_k$.

The two last mentioned are numeric values, and therefore independent of a and b_k. If we put $\left(\frac{pv}{RT}\right)_k = X$ and $\left(\frac{T}{p}\frac{dp}{dT}\right)_k = Y$, we

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calculate α and β from the two equations:

$$Y = \frac{1}{1 - \frac{3}{4}\,\frac{1-\alpha}{1-\alpha-\beta}}$$

$$X = \frac{3}{2}\,\frac{1}{1-\alpha-\beta} - \frac{9}{8}\,\frac{1-\alpha}{(1-\alpha-\beta)^2}.$$

The result is:

$$\alpha = 1 - \frac{2\left(1-\frac{1}{Y}\right)}{XY}$$

$$\beta = \frac{\frac{1}{2} - \frac{2}{Y}}{XY}.$$

If the above considerations are perfectly accurate, then β must be of the order of α, and smaller than α.

In order to calculate b_k we can make use of the equation:

$$b_k = \frac{RT_k}{8\,p_k}\,\frac{1+2\,(\alpha+\beta)}{(1-\alpha-\beta)^2}\,(1-\alpha-4\,\beta).$$

If α and $\beta = 0$, we get the well-known equation:

$$b = \frac{RT_k}{8\,p_k}.$$

By means of the above values of α and β for CO_2, we find:

$$b_k = \frac{RT_k}{6{,}807\,p_k}.$$

From this we calculate $b_k = 0{,}00225$, from which would follow the value of 0,002615 for b_g.

Also by the introduction of the quantities X and Y we should be able to calculate b_k from:

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$$b_k = \frac{RT_k}{p_k}\left(X - \frac{1}{Y}\right).$$

With $X = \frac{1}{3.4}$ and $Y = 6.7$ we calculate:

$$b_k = \frac{RT_k}{p_k}\ \frac{1}{6.9},$$

from which follows that $b_k = 0{,}00222$ and $b_g = 0{,}00258$.

The quantity a may be calculated from the equation:

$$\frac{(RT_k)^2}{p_k} = \frac{64}{27}\, a\, \frac{(1-\alpha-\beta)^4}{(1-\alpha)(1-\alpha-4\beta)},$$

from which we find for a the value of 0,00855. If we introduce the quantities X and Y instead of α and β, we have for the calculation of a the equation:

$$a = \frac{(RT_k)^2}{p_k} X^3 (Y-1).$$

If X and Y are $\frac{1}{3{,}4}$ and 6,7 we find from this for a the value 0,008484, so about 3 percent lower than was assumed for the calculation of the series of values of b.

When determining the critical volume of carbonic acid, we observed (p. 582) that the equations (5) and (4) of p. 580 are not perfectly satisfied, if for f the value 2 and for b_0 the value 0,0007 was assumed.

This might in the first place be owing to the fact that we have to consider equation (4) only as an approximation. But even if we grant this, it remains desirable to investigate in how far such an equation can make the observation and the calculation agree. Therefore I have investigated what values f and b_0 ought to have in equation (4), in order to make the agreement perfect.

This remains a work that requires longer calculations. For this purpose I brought equation (5) of p. 580 under another form. If

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the quantity $\left(\frac{b-b_0}{b_g-b_0}\right)^2$ is represented by x, we find from (4):

$$\frac{v-b}{b_g-b_0}=\frac{\sqrt{x}}{f(1-x)}$$

and

$$\frac{v}{b_g-b_0}=\sqrt{x}\left\{1+\frac{1}{f(1-x)}\right\}+\frac{b_0}{b_g-b_0}.$$

If we put μ for $\frac{b_0}{b_g-b_0}$, then:

$$\frac{v-b}{v}=\frac{1}{1+f(1-x)\left(1+\frac{\mu}{\sqrt{x}}\right)}.$$

Now $\frac{db}{dv}$, for which we found the value:

$$\frac{db}{dv}=\frac{1}{1+f\left[\left(\frac{v-b}{b-b_0}\right)^2+\left(\frac{v-b}{b_g-b_0}\right)^2\right]}$$

can also be given under the following form:

$$\frac{db}{dv}=\frac{1}{1+\frac{1}{f}\frac{1+x}{(1-x)^2}},$$

and so:

$$1-\frac{db}{dv}=\frac{\frac{1}{f}\frac{1+x}{(1-x)^2}}{1+\frac{1}{f}\frac{1+x}{(1-x)^2}}$$

For

$$-\frac{v-b}{2}\frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}=\frac{db}{dv}\frac{f\left[\left(\frac{v-b}{b-b_0}\right)^2+\left(\frac{v-b}{b_g-b_0}\right)^2\right]-f\left(\frac{v-b}{v-b_0}\right)^3 f\frac{(1-x)^2}{1+x}}{1+f\left[\left(\frac{v-b}{b-b_0}\right)^2+\left(\frac{v-b}{b_g-b_0}\right)^2\right]}$$

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we find:

$$-\frac{v-b}{2}\frac{\frac{d^2b}{dv^2}}{1-\frac{db}{dv}}=\frac{\frac{1}{f}\frac{1+x}{(1-x)^2}-\frac{1}{f}\frac{1}{(1-x)(1+x)}}{\left\{1+\frac{1}{f}\frac{1+x}{(1-x)^2}\right\}^2}.$$

If we introduce this value in (5), we get the following equation:

$$\frac{\frac{3}{2}}{1+f(1-x)\left(1+\frac{\mu}{\sqrt{x}}\right)}=\frac{\frac{1}{f^2}\frac{(1+x)^2}{(1-x)^4}+\frac{1}{f}\frac{1}{(1+x)(1-x)}}{\left\{1+\frac{1}{f}\frac{1+x}{(1-x)^2}\right\}^2}$$

or

$$\frac{\frac{3}{2}}{1+f(1-x)\left(1+\frac{\mu}{\sqrt{x}}\right)}=\frac{1+f\left(\frac{1-x}{1+x}\right)^3}{\left\{1+f\frac{(1-x)^2}{1+x}\right\}^2}.$$

Here we have a relation between the 3 quantities f, x and μ. By making use of the value which $\alpha=\frac{db}{dv}$ must have in order to properly represent the critical quantities, we have a relation between f and x. Be:

$$\frac{1}{1+\frac{1}{f}\frac{1+x}{(1-x)^3}}=0{,}132.$$

Then $f\frac{(1-x)^2}{1+x}=0{,}152$ and $\left\{1+f\frac{(1-x)^2}{1+x}\right\}^2=1{,}327.$

We write therefore:

$$\frac{1{,}9905}{1+f\left(\frac{1-x}{1+x}\right)^3}=1+f(1-x)\left(1+\frac{\mu}{\sqrt{x}}\right).$$

If we assume $f=2$, we find $1-x=0{,}358$, and we can calculate μ. With these data we find $\mu=0{,}284$, whereas the equation for b, which we had drawn up, contains for μ the value $\frac{7}{19}=0{,}368$.

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If we had kept this value for μ, we could have calculated f, and we should not have found 2 but about 1,8.

So there is no perfect concordance. Whether this involves that the given equation is only an approximation, or whether the imperfect agreement is the consequence of the certainly not absolute accuracy of the observations, cannot be decided for the present.

So I have to leave unexplained the result furnished by the series of values for b, which are given for $t = 13°,1$. This series agrees accurately with a formula of the given form, which appears from the following values. Take again $f = 2$, but $b_0 = 0{,}0008$, and put $b_g - b_0$ as unknown; then we find, beginning again with the smallest volume:

	v	$b_g - b_0$
Liquid volumes.	0,0020527	0,00165
	20937	164
	21822	1635
	22234	161
	22647	1622
Gas volumes.	12933	1654
	13036	160
	13764	168

Though this proves convincingly, that the liquid portion of the isothermal and the gas portion follow exactly the same equation, it remains unexplained that b_0 is found to be here greater than in the series of values at higher temperature. In reality b_g is 0,00165 + 0,0008 = 0,00245 for this series; but the difference between this value and 0,0026, as it is at a little more than 30°, cannot be explained either.

Finally I will point out a result of the given equation for b. If we write:

$$p + \frac{a}{v^2} = \frac{RT}{v - b_0 - \dfrac{fRT}{p + \dfrac{a}{v^2} + \alpha(b - b_0)}}$$

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or

$$\left(p+\frac{a}{v^2}\right)(v-b_0)+f\,RT\,\frac{\alpha\,(b-b_0)}{p+\frac{a}{v^2}+\alpha\,(b-b_0)}=(1+f)\,RT,$$

it appears that at a very high degree of density, when $\alpha\,(b-b_0)$ will have become but a very small part of $p+\frac{a}{v^2}$, the equation of state tends to:

$$\left(p+\frac{a}{v^2}\right)(v-b_0)=(1+f)\,RT.$$

The condition comes nearer and nearer to such a one for which the complex molecules may be considered as broken up into single atoms. With the disappearance of the atomic forces the mode of motion will naturally tend more and more to a free motion of the atoms in all directions, and so to an amount for the specific heat, as if there were as many molecules, as we else should say atoms. For the liquid state we have no experimental data in this respect. But for the solid state the law of DULONG and PETIT points in that direction. Moreover we have to assume with BOLTZMANN for the solid state, that the specific heat will be found twice as great, on account of the property of a solid body to keep every material point fixed at a certain place. This double amount will, however, not be found for the liquid state.

The amount of $\frac{\alpha\,(b-b_0)}{p+\frac{a}{v^2}}$ is calculated from the equation:

$$\frac{b-b_0}{v-b}=\frac{f\,\frac{RT}{v-b}}{p+\frac{a}{v^2}+\alpha\,(b-b_0)}=\frac{f}{1+\frac{\alpha\,(b-b_0)}{p+\frac{a}{v^2}}}$$

or

$$\frac{\alpha\,(b-b_0)}{p+\frac{a}{v^2}}=f\,\frac{v-b}{b-b_0}-1$$

For $v=0{,}0020527$, $b_0=0{,}0008$ and $f=2$, we find for it a value of nearly 0,275.

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Mineralogy. — Prof. J. L. C. SCHROEDER VAN DER KOLK: "*On hardness in minerals in connection with cleavage.*"

In 1852 KENNGOTT tried to find out the connection between the hardness of minerals on the one hand and their specific gravity and molecular weight on the other. For the purpose he choose corundum and hematite and taking in consideration the molecular weight of the two minerals found the specific gravity of corundum to be very high, comparatively speaking, although practically it was lower than that of hematite. Comparing a great number of other minerals in the same way (taking them in twos) he found the rule, that a mineral which has, as KENNGOTT calls it, the greatest relative specific gravity also has the greatest hardness.

A standard for the relative amount of specific gravity may be found, when dividing this by the figure representing the molecular weight. We shall then find for corundum (the harder mineral of the two) the quotient 0,039, for hematite, it will be no more than 0,033.

In his investigation KENNGOTT has limited himself to minerals, which crystallographically bear great resemblance, of which the composition chemically is analogous and which possess an equal degree of cleavage. This, as we shall see, is of great importance to obtain satisfactory results.

However I thought desirable to try and compare those minerals, which are less analogous. Even though the results should be contradictory, that very fact might open new vista's.

A first trial with the elements, in which the specific gravity had to be divided by the atomic weight was not unsatisfactory.

Diamond, by far the hardest substance proved also to yield the largest quotient (compactness) i.e. 0.293; the only substance, which somehow comes near to it is crystalline borium, the quotient being 0.245. Good results I also obtained among others, with the following metals: nickel (0,147), manganese (0,145), iron (0,141), chromium (0,133), iridium (0,119), platinum (0,109), gold (0,098), lead (0,055), sodium (0,042), potassium (0,022) etc. I shall later speak of some few exceptions which, as we shall then see, are however only apparent ones: instances of these apparent exceptions are beryllium (0,233) and copper (0,141).

When however we compare the quotients with those we obtain with corundum and hematite, they seem contradictory; for corundum a very hard substance, we found 0,039, for lead (a soft substance) a higher figure 0,055. A moment's consideration however, will lead

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us to conclude, that it won't do, in the one case, to divide by the figures representing the atomic weight, in the other by those representing the molecular weight; instead of dividing by the latter, we must do so by the average atomic weight $\frac{m.\ g.}{n.}$ [1]) or, which comes to the same, multiply the quotient we obtained, (with the molecular weight as divider) with the number of atoms of the molecule. Then we can better compare the results; for corundum multiplied with 5 yields the very high quotient 0,195; hematite that of 0,165.

On further trial, I found, that hydroxyl, in the topaz for instance, isomorphously, as it is called, replaced by fluor, must in our calculation be treated as one single atom; the same holds for NH_4 in salmiak.

300 minerals I have submitted to this calculation, as will be more fully expounded on in a treatise, for the moment I left unconsidered the zeolithes and such like minerals.

Truly, by multiplying with the atom-number, we have in a great measure, added to the possibility of comparing minerals, but still the first list of results looks far from promising; for a mineral, which is generally known for its soft substance, such as graphite, yields the high quotient 0,188, whereas talc, which is known for the same quality has for quotient 0,141, just as iron. On the other hand quarz, known for its hardness, yields the comparatively low quotient 0,132. Still, too many good results were obtained, to give up further trial.

In order better to overlook the matter, I have arranged the minerals according to their quotient making use of the scale of MOHS to state the respective hardness, however not in figures but by a sort of ordinates. The tops of these ordinates may be joined and by doing so, we get a peculiar zig-zag line, which gets lower as the quotients diminish: consequently the hardness on the whole, diminishes with the quotient. The irregular zig-zag line however shows, that there are still disturbances, which we have not taken in account, but then these disturbances are explained, when we consider cleavage a factor, for in the minima we find the minerals known for their perfect cleavage, in the maxima those known for imperfect cleavage. [2]).

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[1]) n = number of atoms in the molecule.

[2]) Besides the faculty of more or less perfect cleavage the number of directions is of significance. For when a cleavage-plane is rich in molecules, the richness will decrease with the number of the cleavage-planes. With an indefinite number of cleavage-directions practically not a single cleavage plane would stand out for richness

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This rule holds till the maxima on the zig-zag line fall below the hardness 5 (MOHS). From that moment all regularity stops.

The cause of this new disturbance is soon found, when we look for the minerals on the scale of MOHS. It then appears that the mutual position of the highest 5 degrees of MOHS remains on the whole the same on the list, that on the other hand the lowest five minerals on the scale of MOHS (those of the hardness 5 and lower) are scattered all over our list in irregular order. The condition of hardness of the lowest degrees of MOHS is only apparent, the results of more or less perfect cleavage, so for instance number 1 of MOHS admits of cleavage only in one direction, number 2 in two, number 3 in three and number 4 in four [1]). So we should distinguish between two sorts of hardness, a theoretical one, which will principally depend upon the quotients and an experiment, one which in a high degree depends on cleavage.

It is true not one single metal can practically reach its theoretical hardness, so we must consider it to be the limit which — the quotient given — experimental hardness can approach; still theoretical hardness is a quantity, which is important.

For since on the one hand we have found, that cleavage may in a high degree lower experimental hardness, there are on the other hand phenomena showing, that an inpediment of cleavage may considerably increase the quality hardness. The cases are perhaps not numerous, but they are not lacking.

For instance biotite, a mineral known for its perfect cleavage, almost entirely loses that faculty and changes into so-called rubellane, but then the hardness increases. Something of the same kind we see happening in talc, which by heating loses its cleavage and gets considerably harder. Also inclusures of foreign minerals, though ever so few may impede cleavage. The microscope shows many instances. I. e. amphibole, which is of perfect cleavage, is often interspersed with apatite-needles, which here more or less act the part of nails and prevent cleavage. What makes the phenomenon peculiar is, that

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of molecules and we should have to deal with a substance that admits of no cleavage-directions. A substance with 4 or 6 cleavage-directions, in hardness experiments, comes to the same with a material of imperfect cleavage; in a smaller degree this is the case in cubic cleavage, in a still smaller degree in rhombohedral cleavage and in the smallest degree in cleavage, in one single direction.

[1]) This faculty of cleavage acts a great part in all researches, undertaken to find out the experimental hardness. Consequently the succession of the scale of MOHS has remained unaltered both when experimenting with the sklerometer as with the boring-methods of PFAFF or with the pressure of a lens against a plane (AUERBACH).

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the addition need be but very small and the degree of hardness not very great: the question here is only to impede cleavage or gliding.

But then similar phenomena we know excellently well in alloys, in which very small additions may considerably increase the hardness of the main substance, and these additions in themselves need not be very hard. This is a known fact of iron, but the quotient of copper (its theoretical hardness) is equally great as that of iron; so copper by the addition of small quantities of other elements must be able to acquire not only the hardness of iron, but also that of steel. So by these additions we must impede cleavage or gliding in copper. For this purpose it is preferable to choose elements, which are not too near akin to copper, because they may possess the same cleavage or form an isomorphous mixture.

What has been said of copper as a matter of course, holds for all metals, not one, as we may say, entirely lacking cleavage or translation. So not a single metal will reach its theoretical hardness. In the first place however this may be said of the metal beryllium, which yields the very high quotient 0,233. According to its quotient (theoretical hardness) it should be able to attain an experimental hardness, which greatly exceeds that of steel.

Astronomy. — *On the luminosity of the fixed stars.* By Prof. J. C. KAPTEYN.

1. *Mean parallax of stars of determined magnitude and proper motion.*

In a paper published elsewhere [1]) I found for the mean parallax $\bar{\pi}_{\mu,m}$ of stars of a determined proper motion μ and a determined magnitude m (Potsdam system) the formula

$$\bar{\pi}_{\mu,m} = \varepsilon^{m-55}\sqrt[p]{A\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values of the constants were derived as well for the whole of the stars as for the stars of the first and second spectral type (Secchi's notation) separately.

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[1]) Publ. of the Astr. Labor. at Groningen No. 8, On the mean parallax of stars of determined proper motion and magnitude.

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I found

	Type I.	Type II.	All the stars.	
A	0.116	0.0262	0.0387	
p	1.11	1.54	1.405	. . (2)
ε	0.905	0.905	0.905	

The spectra were there, as they are in this paper, taken from Pickering's „Draper Catalogue". Exceptions to this rule will be expressly stated. This catalogue will be denoted by the letters D.C. The relation (1) was derived:

1st From directly measured parallaxes, almost exclusively using the longest and most reliable series of such measures.

2nd From the mean parallax of stars of different magnitudes, according to the determination which was communicated to the Academy in the meeting of October 1897 [1]).

A further confirmation of the values of the parallax given by formula (1) for the stars with extremely small proper motions was found in the strong condensation towards the milky way of the bright stars with very small proper motions (see Proceedings Jan. 1893), as compared with the condensation for the whole of the fainter stars.

The values for type I are, comparatively speaking, very uncertain. This is explained by the fact that for this type large proper motions are exceedingly scarce, in consequence of which the parallaxes of very few stars of this type, and these exclusively very bright ones, have been directly determined.

For type II the circumstances are much more favourable. Still the values given for this type and for the whole of the stars must only be considered as preliminary results, which may be altered somewhat by the here following considerations.

2. *Probability that a star's parallax exceeds its mean value in a given proportion.*

In the paper quoted I also tried to derive the probability that the parallax of any arbitrarily chosen star shall exceed its mean

[1]) The only alteration made in the figures there given is a small correction, which has been applied to the mean magnitude of the stars 0—3.5, in order to bring them in better accordance with the best photometric determinations.

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value, computed by formula (1), in a given proportion. This determination, which necessarily must be very rough, was based on the hypothesis that the quantities

$$z = log \frac{\pi}{\pi_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where π is the true, and π_0 the *probable* parallax, are distributed according to the law of errors.

By this hypothesis the determination of the required probability was reduced to the derivation of a single quantity, for which the probable amount (ϱ) of z was chosen.

The relations between the probable parallax π_0 and the mean parallax $\bar{\pi}$ is given by the formula

$$\pi_0 = \bar{\pi} . e^{-\frac{\rho^2}{4\, mod^2\, (0.47694....)^2}} = \bar{\pi} . e^{-5.827\rho^2} \quad . \quad . \quad . \quad . \quad (4)$$

The value of ϱ was derived from the observed parallaxes in different ways. The value which was finally adopted is

$$\varrho = 0.19 \pm 0.02 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Introducing this value, (4) becomes

$$\pi_0 = 0.810\, \bar{\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The true uncertainty of this value of ϱ is somewhat larger probably than is indicated by the p. e.; it can not be doubted however that the true value of ϱ must be very small. It thus appears that the proper motion, combined with the magnitude of a star, affords a very good criterion of its distance. It is not difficult by means of the value (5) of ϱ to compute a table giving the probability that the parallax of an arbitrarily chosen star exceeds a times its mean value $\bar{\pi}$. Such a table is given in the paper quoted above. It appears that the probability is 0.5 that the parallax of a star taken at random shall be included between

$$0.523\ \bar{\pi} \text{ and } 1.255\ \bar{\pi} \text{ or between } \frac{\pi_0}{1.55} \text{ and } 1.55\ \pi_0,$$

where π_0 is the probable parallax computed by the formulae (1) and (6).

The accuracy of all these determinations (with the exception perhaps of those for type I) is already so considerable as to justify

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an attempt to determine from these data, combined with the known number of stars of determined magnitude and proper motion, the number of stars of determined apparent magnitude within a given distance from the solar system, and from these numbers again to conclude the relative frequency of stars of determined absolute luminosity.

3. *Data for proper motion, magnitude, and number of stars of a given magnitude.*

For the northern hemisphere the necessary data about the proper motions of stars brighter than 6.5 can be derived from AUWERS BRADLEY.

To the proper motions derived from this source I have applied the following corrections:

a. A correction originating in a correction to the constant of precession of — 0.000446 of its amount.

b. A correction to the motions in declination of —0″.008 for declinations south of + 51° 30′ and of — 0″.001 for more northern declinations.

These values of the corrections are not yet the best which can be derived, but they differ very little from them. For the fainter stars the data about proper motions are much more uncertain.

Still I think I have succeeded in collecting even for these stars such data as will suffice to furnish a good check on the results derived from the brighter ones.

To derive data for the number of stars of a given magnitude the following sources were used:

a. Gore. The hundred brightest stars. Knowledge Sept. 1900 p. 202.

b. Kobold. (Vierteljahrsschr. der A. G. Vol. 34 p. 213).

From these two sources I could derive directly the numbers of stars of different magnitudes up to 5.5, according to photometric determinations. A correction of + 0 m 17 (see Potsdam Obs. Vol. 13, p. 459) has been applied to reduce the Harvard results to the Potsdam scale.

c. For fainter stars the data of the B. D. were used. The corrections which are necessary to reduce the magnitudes of this work to the Potsdam scale are now known with tolerable accuracy. For the magnitudes 3.0—7.0 these corrections are given in the Potsdam D. M. (Potsd. Obs. Vol. 13, p. 454); for the magnitudes 6.5—9.0 by the investigations of SEELIGER (Betracht. üb. die raümliche Vertheilung der Fixsterne. Abh. der K. bayer. Ak. der Wiss. 2e Cl. 19er Bd. 3e Abth. S. 21). The mean was taken of SEELIGER's values for the declinations 0°—49°. SEELIGER's data, when reduced to the

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Potsdam scale, agree very well with the values which have been found in Potsdam for the magnitudes 6.5 and 7.0.

From all these data I find the following comparison of the magnitudes of the B. D. with the Potsdam photometric magnitudes. For the latter we have as is well known

$$\log \frac{\text{intensity of star of mag } m}{\text{intensity of star of mag } m+1} = 0.4. \quad . \quad . \quad (7)$$

BD.	Potsdam.	
3.0	3.38	
4.0	4.25	
5.0	5.08	
6.0	6.01	
6.5	6.59	
7.0	7.13	. . . . . (8).
7.5	7.68	
8.0	8.18	
8.5	8.77	
9.0	9.37	

It was assumed that the magnitudes of AUWERS BRADLEY are homogeneous with those of the B.D.

For the numbers of stars I find from the just mentioned sources, after a careful reduction to rounded off values of the magnitude according to the Potsdam scale:

Potsd. mag.	total	Typ. $I + II$ only.	
brighter than 1.50	18	17	
1.50—2.50	51	47	
2.50—3.50	145	133	
3.50—4.50	466	456	
4.50—5.50	1 508	1 476	. (9)
5.50—6.50	4 944	4 839	
6.50—7.50	15 370	15 043	
7.50 - 8.50	45 530	44 561	
8.50—9.50	153 830	150 557	

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The numbers of stars belonging exclusively to the first and second spectral types, which are given in the last column were derived: for the magnitudes 0—3.5 from Mc. CLEAN's determinations; for the other magnitudes by multiplying the numbers of the foregoing column by $\frac{46}{47}$.

This ratio was found by actual countings in the D.C.

4. *Numbers of stars whose proper motion is included between given limits.*

In the following table are given the numbers of stars which I found between different limits of proper motion and magnitude. The reason why not the total numbers, but only those for types I and II are given, is simply that the latter could be more easily derived from other countings which had previously been made. The difference is practically of no importance for the present investigation.

The stars brighter than 1.5 are entirely omitted; of all these stars the parallaxes have been measured. For the formation of the following tables they can be taken directly from the observations.

Magnitudes 1.5—3.5. The proper motions were taken from NEWCOMB's Fundamental Catalogue. The spectra of those stars, which are too far south for the DC. were taken from Mc. CLEAN's *Spectra of Southern Stars* (London 1898).

Magnitudes 3.5—6.5. The corrected proper motions of AUWERS BRADLEY [1]) were counted, the magnitudes having been previously corrected by (8). In all there appeared to be of the magnitudes 3.6—4.5, 4.6—5.5 and 5,6—6.5 respectively 297, 652 and 1017 stars. Thus, in order to get the numbers (9) for the whole of the sky, the numbers of stars in BRADLEY had to be multiplied by the the respective factors 1.535, 2.264 and 4.756. (Consequently to get the numbers of stars which are actually in BRADLEY, the numbers of Table 1 must be divided by these same factors).

Magnitudes 6.5—9.5. Different sources (AUWERS BRADLEY, AUWERS *A G C*, BOSS *A G C*, PORTER's catalogue of proper motions, combined with countings in the catalogues of LALANDE and BESSEL) were consulted to determine what fraction the numbers of the stars with proper motions 0″00—0″10, 0″10—0″15, 0″15—0″20 . . . . .

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[1]) Rejected were all the stars which have been incompletely observed by BRADLEY, and a few others. There remained 2640 stars in all.

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TABLE 1. Number of stars Type I + Type II in the whole sky.

μ	Mag. / Mean μ	1.5–2.5	2.5–3.5	3.5–4.5	4.5–5.5	5.5–6.5	6.5–7.5	7.5–8.5	8.5–9.5
		2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1
0″.000—0″.009	0″.005	6	5	22	90	343	1504	9010	38257
.010— .019	.015	4	15	52	194	638	1896	7313	28184
.020— .029	.025	1	10	41	177	595	1910	5852	21225
.030— .039	.035	3	16	27	188	542	1910	4768	15809
.040— .049	.045	3	12	27	93	461	1499	3877	12045
.050— .059	.055	5	13	22	86	357	1249	3342	9184
.060— .069	.065	1	4	25	77	252	963	2540	6775
.070— .079	.075	2	2	18	71	247	752	1827	4968
.080— .089	.085		5	25	45	209	692	1337	3614
.090— .099	.095	1	9	17	54	200	646	802	2409
.100— .149	.125	5	10	57	152	424	963	1649	4373
.150— .199	.175	5	9	34	79	181	420	1070	2033
.200— .299	.25	5	11	32	73	200	315	670	919
.300— .399	.35	1	3	17	43	105	75	178	492
.400— .499	.45		5	12	18	34	121	133	196
.500— .599	.55	1	3	8	7	24	38	53	60
.600— .699	.65	2		2	7	5	24	32	36
.700— .799	.75			9	5	10	17	27	26
.800— .599	.85	1		3	2		12	13	16
0.900— 0.999	0.95				2		6	9	10
1.000— 1.199	1.1		1	3	5		7.5	9	10
1.200— 1.399	1.3			3	2	5	13.0	9	7.6
1.400— 1.599	1.5				2		4.5	4.4	6.0
1.600— 1.799	1.7						1.5	4.4	1.5
1.800— 1.999	1.9			2	2		1.5	0.0	1.5
2.000— 2.999	2.5		1				6.0	8.9	6.0
3.000— 3.999	3.5					5	3.0	4.5	6.0
4.000— 4.999	4.5				2		1.5		3.0
5.000— 5.999	5.5					5		4.5	
6.000— 6.999	6.5						1.5		4.5
7.000— 7.999	7.5								
Total		46	134	458	1476	4842	15042	44576	150607

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are of the whole number of all the stars. The subdivision of the proper motions 0″000—0″100 was then made by the aid of certain plausible conditions, which are certainly or probably fulfilled by the numbers of small proper motions. Further explanation about this point will be given in a subsequent more detailed publication. The numbers given in the table were derived by multiplying the total numbers (9) by the fractions which have been found in this way.

In order to simplify the computations without sensibly impairing the accuracy, all the stars of which the magnitude is between 3.5 and 4.5 between 4.5 and 5.5 etc., were reckoned to be of magnitude 4.1 [2]) respectively 5.1 etc. Similarly for all the proper motions between 0.″000 and 0.″009; 0.″010 and 0.″019 etc. the mean proper motions 0.″005, 0.″015 etc. were substituted.

For each magnitude and each proper motion occurring amongst the arguments of table 1, the mean parallax was now computed by the formula (1). I thus found *e. g.* for

$$\text{p. m. } 0''045, \quad \text{mag } 6.1, \quad \bar{\pi} = 0''0102,$$

which value thus represents the mean parallax of the 461 stars of which according to table 1 the p. m. and magnitudes are included between the limits 0″040 and 0″050, respectively $5^m,5$ and $5^m,6$. By the aid of the table which was quoted above it is now easy to compute the number of stars amongst these 461, of which the true parallaxes are included between given limits. We thus find:

---

[2]) If the number of stars of magnitude m or brighter is $A_m = K. a^m$, then the mean magnitude $\bar{m}$ of the stars, whose apparent magnitudes are included between the limits m and m + 1, will be $\bar{m} = m - \frac{1}{l\,a} + \frac{a}{a-1}$. For photometric magnitudes I find in the mean $a = 3.266$. This gives $\bar{m} = m + 0^m\,596$, for which I have taken $m + 0.6$.

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Limits of π	fraction of the whole	Number.
0″00000 and 0″00100	0.001	0
00100 » 00158	.004	2
00158 » 00251	.028	13
00251 » 00398	.097	45
00398 » 00631	.209	96
00631 » 0100	.275	127
0100 » 0158	.226	104
0158 » 0251	.116	54
0251 » 0398	.0358	16.5
0398 » 0631	.0068	3.1
> 0″0631	.0009	0.4
	1.000	461

Repeating the same computations for all the numbers of table 1, the following summary is obtained [1]).

In the second column are given the mean parallaxes $\bar{\pi}$, which were computed by the formula

$$\frac{5}{3}\frac{1}{\bar{\pi}} = \frac{\frac{1}{\pi_2^5} - \frac{1}{\pi_1^5}}{\frac{1}{\pi_2^3} - \frac{1}{\pi_1^3}} \quad \ldots\ldots\ldots \quad (10)$$

The mean parallax $\bar{\pi}$ given by this formula satisfies the condition that the absolute magnitude (see next §) computed from it corresponds to the mean of the absolute magnitudes of all the stars whose parallaxes have values between π_1 and π_2.

In the last column are given the volumes of the spherical layers

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[1]) A similar table was published by me last year. (Publ. of the Astr. Lab. at Groningen, No. 1, p, 93). Since that time I found occasion to repeat the whole investigation with greater care, so that the present results must be considered as more trustworthy.

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TABLE 2. Number of parallaxes in the whole sky (Type I + Type II).

π	Mag. / $\bar{\pi}$	—0.9	0.1	1.1	2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1	Vol.
0″.00000—0″.00100					0.4	0.5	3.0	18.0	84.0	440.0	3016.0	15363.8	
.00100— .00158	0″.00118				1.0	2.0	8.0	34.0	152.0	667.0	3658.0	16197.0	3 140 000
.00158— .00251	.00187			1	1.9	2.7	15.2	76.0	306.0	1216.0	5419.0	21953.0	788 000
.00251— .00398	.00296				2.9	7.9	29.1	141.0	531.0	1942.0	6912.0	25578.0	198 000
.00398— .00631	.00460				3.8	14.9	48.7	211.0	770.8	2642.0	7880.0	26044.0	49 700
.00631— .0100	.00743	1	I	1	5.1	20.2	64 7	255.5	901.0	2899.7	7352.0	20977.0	12 500
.0100 — .0158	.0118				6.1	23.7	74.6	248.8	833.5	2403.2	5278.5	14067.5	3 140
.0158 — .0251	.0187				7.3	21.8	74.5	209.4	614.3	1556.9	3003.9	6789.5	788
.0251 — .0398	.0296			2	6.5	17.6	59.2	142.4	367.5	780.5	1338.0	2568.4	198
.0398 — .0631	.0469		1	2	5.2	11.5	40.1	78.8	177.2	322.5	496.4	792.1	49.7
.0631 — .0100	.0743		1	1	3.3	6.4	23.3	37.7	69.1	114.6	157.3	207.9	12.5
.0100 — .158	.118		1	1	1.6	3.0	11.4	15.3	22.9	39.2	45.8	50.0	3.14
>.158	.204	1	1	2	0.9	1.8	6.2	8.1	12.7	18.4	19.6	18.8	1.05
		2	5	10	46.0	134.0	458.0	1476.0	4842.0	15042.0	44576.5	150607.0	

included between two spheres of which the radii correspond to the parallaxes of the first column. As unit of volume I took the volume of a cube, of which the side is the distance corresponding to a parallax of 0″1. The numbers entered in the columns of the apparent magnitudes —0.9, 0.1 and 1.1 show simply the number of stars whose *measured* parallax lies between the corresponding limits in the first column.

6. *Absolute luminosity and absolute magnitude.*

As unit of luminosity I will adopt the total luminosity of the sun. It is true that our knowledge of the relation between the quantities of light which we receive from the sun and from certain fixed stars is still very imperfect. This is however of little importance, because, when this relation will be better known, it will only be necessary to multiply all our results by a certain constant, in order to bring them into accordance with the new determination.

I will here adopt: light of the sun = 40.000.000.000 × light of Vega [1]). According to the Potsdam measures the apparent magnitude of Vega is 0.41. From these data it can be easily derived that the sun, when transferred to a distance corresponding to the parallax $\pi = 0''10$, would have the apparent magnitude 5.48. I will adopt $5^m,5$, which accidentally agrees exactly with the mean magnitude of the Bradley stars. If we put further:

L = luminosity, or total illuminating power of a star of apparent magnitude m and parallax = π,

we find easily by the relation (7):

$$\log L = 0.2000 - 0.4\, m - 2 \log \pi \ldots\ldots \quad (11)$$

We further define the *absolute magnitude* (M) of a star, of which the parallax is π and the distance r, as the apparent magnitude which that star would have if it was transferred to a distance from the sun corresponding to a parallax of 0″1. It is easily seen that

$$M = m - 5 \log r = m + 5 + 5 \log \pi = 5.5 - 2.5 \log L \quad . \quad (12)$$

For the sun $L = 1$; the formula thus gives for the absolute magnitude of the sun $M = 5.5$, in accordance with what has been said above.

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[1]) Young, General Astronomy p. 213.

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TABLE 8. Log. number of stars per unit of volume.

Mean π	r	$M.$ / log. L	−7.55	−6.55	−5.55	−4.55	−3.55	−2.55	−1.55	−0.55	0.45	1.45	2.45	3.45	4.45	5.45	6.45	7.45	8.45	9.45	10.45	Density.
			5.22	4.82	4 42	4.02	3.62	3.22	2.82	2.42	2.02	1.62	1.22	0.82	0.42	0.02	9.62	9.22	8.82	8 42	8.02	
0".00118	84.7		3.51	3.81	4.40	5.033	5.685	6.326	7.068	7.713												0.122
.00187	53.5		4.11	4.38	4.53	5.286	5.984	6.589	7.188	7.838	8.446											0.234
.00296	33.8				5.18	5.60	6.167	6.852	7.428	7.992	8.543	9.111										0.418
.00469	21.3					5.88	6.477	6.991	7.628	8.190	8.726	9.201	9.719									0.656
.00743	13.5			5.90	5.90	5.90	6.613	7.209	7.714	8.310	8.858	9.366	9.769	0.225								0.869
.0118	8.47							7.28	7.878	8.377	8.899	9.423	9.884	0.225	0.651							0.985
.0187	5.35								7.97	8.441	8.975	9.423	9.892	0.295	0.580	0.935						1.031
.0296	3.38								8.00	8.52	8.949	9.476	9.857	0.269	0.596	0.830	1.113					1.000
.0469	2.13								8.32	8.60	9.021	9.364	9.907	0.200	0.552	0.812	0.999	1.202				0.917
.0743	1.35									8.90	8.90	9.422	9.709	0.270	0.479	0.742	0.962	1.100	1.220			0.829
.118	0.85										9.51	9.51	9.71	9.980	0.560	0.688	0.863	1.097	1.164	1.201		0.742
.204	0.49										9.98	9.98	0.219	0.004	0.173	0.663	0.864	1.041	1.210	1.266	1.257	0.648

7. *Derivation of the star-density and the luminosity-curve.*

By the aid of (11) and (12) table 2 can be so altered that the argument: apparent magnitude is replaced by the argument log L or M.

If this is done, and if further the numbers of the table are divided by the volumes given in the last column and logarithms are taken, we get the following table: (p. 669)

The numbers of the last row of this table require some explanation. If this row had been derived in the same way as the others the resulting numbers would have been those corresponding to the values 1.94, 1.54, 1.14 ... etc. of log L. For the sake of uniformity I derived from these, by interpolation between the logarithms, the values corresponding to the values 2.02, 1.62, 1.22 ... etc. of log L.

It is still possible to enter this table with the argument: apparent magnitude; for the logarithms belonging to the same apparent magnitude are now placed in an oblique line descending towards the right. In order to facilitate such an entering of the table, the logarithms belonging to the apparent magnitudes 3.1—7.1 have been included between heavy lines. This enables us to judge more readily of the weight of the several numbers tabulated. Thus it is seen at once that the numbers which are in the table to the left of the heavy lines must have a very small weight because they are relative to the stars of the magnitudes 2.1, 1.1 ... which are exceedingly few in number. Similarly, though for a different reason, the numbers which are outside the heavy lines on the right hand side, and which belong to the magnitudes 8.1 and 9.1, have a small weight, at least for the smaller values of the parallax.

The table virtually is nothing else than a table for the logarithms of the relative densities of stars of different absolute magnitudes (or absolute luminosity). The absolute density, *i. e.* the *total* number of stars per unit of volume, can not be determined of course, because we know nothing about the very faintest stars. We can however determine that density expressed in its value at a certain distance from the sun as unit.

For this distance I will provisionally adopt the distance corresponding to a parallax of 0".0296. I will adopt the hypothesis that the luminosity-curve is the same for different distances from the sun. Luminosity-curve I call the curve which for every absolute magnitude gives the number of stars per unit of volume, or in other words, which gives the proportion in which the stars of different apparent magnitudes would be distributed over the sky, if they were all placed on the surface of the sphere whose radius corresponds to the paral-

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lax 0"1. In the following tables I will give not the numbers of stars of each absolute magnitude, but the logarithms of these numbers. As a consequence of the hypothesis which has been mentioned the ratio of the *absolute* densities is necessarily the same as that of the densities for the separate absolute magnitudes.

If the density was constant, the numbers in each vertical column of table 3 should be identical. For the middle of the table this condition is roughly satisfied; for the large and for the small distances however it is not.

The manner in which the densities given in the last column are determined, is perhaps best explained by an example.

The number of stars (not the logarithm) per unit of volume for the stars of the four absolute magnitudes -6.55, -5.55, -4.55, -3.55 together is:

for $\pi = 0''00118$, (app. mag. 2.5—6.5) 0.000 0623
" " $= 0''00187$, (app. mag. 1.5—5.5) .000 1215

We thus get for the ratio of the densities Δ_1 and Δ_2

$$\frac{\Delta_1}{\Delta_2} = 0.513$$

As a second determination we have for the stars of the absolute magnitudes -6.55 to -2.55:

for $\pi = 0''00118$ (app. mag. 2.5—7.5) 0.000 2743
" " $= 0''00187$ (app. mag. 1.5—6.5) 0.000 5095

from which we get

$$\frac{\Delta_1}{\Delta_2} = 0.538.$$

The mean was taken of the two values 0.518 and 0.538, giving to the first value (which depends chiefly on the stars of the apparent magnitudes 6.1 and 5.1) twice the weight of the second value (which depends chiefly on the stars of the apparent magnitudes 7.1 and 6.1).

In the same way the ratio was found of the densities at consecutive distances from the sun ($\pi = 0''00118$, $0''00187$, $0''00296$ etc.) These ratios, together with the adopted density 1.0 for the distance corresponding to a parallax of $0''0296$, gave the values of the last column of table 3.

If now from the logarithms of each row of the table we subtract the corresponding logarithm of the density, or in other words, if the whole is reduced to the density for $\pi = 0''0296$, the following table is derived:

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TABLE 4. Log. number of stars per unit of volume, reduced to $\pi = 0''.0296$.

Mean π \ $M.$ (log. $L.$)	−7.55	−6.55	−5.55	−4.55	−3.55	−2.55	−1.55	−0.55	0.45	1.45	2.45	3.45	4.45	5.45	6.45	7.45	8.45	9.45	10.45
	5.22	4.82	4.42	4.02	3.62	3.22	2 82	2.42	2.02	1.62	1.22	0.82	0.42	0.02	9.62	9.22	8.82	8.42	8.02
0″.00118	4.42	4 72	5.31	5.947	6.599	7.240	7.982	8.627											
.00187	4.74	5.01	5.16	5.917	6.615	7.220	7.819	8.469	9.077										
.00296			5.56	5.98	6.546	7.231	7.807	8.371	8.922	9.490									
.00469				6.06	6.660	7.174	7.811	8.373	8.909	9.384	9.902								
.00743		5.96	5.96	5.96	6.674	7.270	7.775	8.371	8.919	9.427	9.830	0.286							
.0118						7.29	7.885	8.384	8.906	9.430	9.891	0.232	0.658						
.0187							7.96	8.428	8.962	9.410	9.879	0.282	0.567	0.922					
.0296							8.00	8.52	8.949	9.476	9.857	0.269	0.596	0.830	1.113				
.0469							8.36	8.64	9.059	9.402	9.945	0.238	0.590	0.850	1.037	1.240			
.0743								8.98	8.98	9.503	9.790	0.351	0.560	0.823	1.043	1.181	1.301		
.118									9.64	9.64	9.84	0.110	0.690	0.818	0.993	1.227	1.294	1.331	
.204									0.17	0.17	0.41	0.19	0.361	0.851	1.052	1.229	1.398	1.454	1.445
Mean.	(4.42)	4.72	5.27	5.943	6.601	7.222	7.809	8.376	8.920	9.431	9.879	0.264	0.583	0.830	1.024	1.229	1.398	(1.45)	(1.44)
	(4.38)	4.68	5.27	5.931	6.589	7.215	7.806	8.372	8.909	9.410	9.863	0.261	0.601	0.857	1.048	1.239	1.408	(1.46)	(1.45[5])

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The numbers given in this table evidently define what we have called the luminosity-curve.

In taking means the following weights were given:

A. In the columns of abs. mag. —6.55, —5.55..... to + 0.45

B. „ „ „ „ „ „ 1.45, 2.45.....8.45

apparent magnitude	*A.*	*B.*
brighter than 2.5	0	0
3.1	2	2
4.1	5	5
5.1	14	7
6.1	21	7
7.1	3	1
fainter than 7.5	0	0

These weights are roughly proportional to the numbers of stars in BRADLEY which have contributed to the formation of the numbers of table 4.

It is evident that the final means depend only in a very small measure on the values which were found for the densities. They can be derived quite independently of these densities. So we find *e. g.* directly from table 3 for

$$\log \frac{\text{number of stars of absol. mag. } -1.55}{\text{„ „ „ „ „ „ } -2.55}$$

the following values (the assigned weights are added in brackets)

0.599 (3)
0.576 (5)
0.637 (3)
0.505 (1)

Mean. 0.591.

If in the same way the ratios are derived of the numbers of stars belonging to any two consecutive magnitudes, it is only necessary, for a complete knowledge of the luminosity-curve, to derive the number of stars per unit of volume for *one* absolute magnitude. This number was obtained by effecting the best possible agreement with

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the curve which has already been found. The resulting values are given in the last row of table 4. It will be seen that the discrepancies of the values derived by the two methods are very small.

8. *Influence of the uncertainty of the constants of formula* (1).

In order to investigate in how far the values here derived are affected by uncertainties in the fundamental quantities ϱ, ε, π_{55}, I have altered these quantities by amounts which are almost certainly outside (in some cases *far* outside) the limits of the true uncertainties.

As far as the values of π_{55} (i. e. the mean parallax of stars of mag 5.5 and p. m. μ) are concerned, the principal causes of uncertainty are: 1st. the remaining uncertainties in the measured parallaxes and 2nd. the remaining uncertainty in the linear velocity of the sun, by the aid of which the mean secular parallaxes derived from the parallactic motion were reduced to parallaxes in the usual acceptation of the word.

Now it is evident that, if every parallax is multiplied by the same factor not much different from unity, then also all densities will be multiplied by a certain constant factor not much different from unity. Thus, if provisionally we do not aim at the most refined precision in the absolute values of the densities, it is clear that we can make these two uncertainties to bear either wholly on the large and directly determined parallaxes, or wholly on the small parallaxes derived from the parallactic motion.

I chose the latter course, and consequently I took care that the directly measured parallaxes were as well represented by the new formula as by the old one.

In deriving the formula (1) the value[1]) $h = 16.7 \pm 1.15$ kilometer per second was used for the velocity of the solar system. A few months[2]) ago CAMPBELL, derived from the material given by his own observations, which is much more extensive than that from which the above value was derived, the value $h = 19.9 \pm 1.52$ kilometer. For the mean linear velocity of the stars he finds 34.1 kilometer. From this latter value we get, by the method explained in Proceedings October 1897, another value, which cannot differ much from $h = 18.3$. As the final value from CAMPBELL's observations we must thus adopt about $h = 19.0$. Everything considered the value:

[1]) Proceedings October 1897.

[2]) Astrophys. Journ. Jan. 1901, p. 81 599.

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$$h = 18.45. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

appears to me to be the most probable value which can at present be adopted.

I now derived anew the values of $\pi_{\mu m}$ in formula (1) in the following suppositions, to which I add the constants which were formerly found (sol. I):

Sol.	h	A	p	ε	ρ
I	16.7	0.0387	1.405	0.905	0.19
II	16.7	0.0387	1.405	0.905	0.00
III	16.7	0.0387	1.405	1.000	0.00
IV	20.2	0.0454	1.30	0.905	0.19
V	18.45	0.0419	1.355	0.87	0.19

(14)

In these solutions the stars fainter than 2.5 and in some of them also those brighter than 7.5, which have no influence on the result, were, for brevity's sake, omitted.

These different solutions give for the densities (Δ):

TABLE 5. Density Δ.

π Limits.	π Mean.	I	II	III	IV	V
0″.00100 —0″.00158	0″.00118	0.122			0.187	0.162
.00158— .00251	.00187	0.234			0.345	0.292
.00251— .00398	.00296	0.418	0.223	0.184	0.568	0.465
.00398— .00631	.00469	0.656	0.592	0.571	0.789	0.684
.00631— .0100	.00743	0.869	1.072	1.294	0.968	0.852
.0100 — .0158	.0118	0.985	1.191	1.507	1.040	0.945
.0158 — .0251	.0187	1.031	1.122	1.403	1.050	0.984
.0251 — .0398	.0296	1.000	1.000	1.000	1.000	1.000
.0398 — .0631	.0469	0.917	1.045	0.889	1.007	0.980
.0631 — .100	.0743	0.829	0.771	0.497	0.875	0.957
.100 — .158	.118	0.742	0.728	0.406	0.813	0.933
> 0.158	.204	0.648	0.627	0.220	0.780	0.929

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For the luminosity-curve we find (after adding to the values I, II and III the constants -0.081, $+0.056$ and -0.104)

TABLE 6. Luminosity-curve.
(Log. number of stars per unit of volume for $\pi = 0''.0296$).

Log. *L.*	*M.*	I — 0.081	II + 0.056	III — 0.104	IV	V
5.22	— 7.55	(4.34)				
4.82	— 6.55	4.64			4.65	4.60
4.42	— 5.55	5.19	(5.71)	(5.82)	5.29	5.17
4.02	— 4.55	5.862	5.71	5.94	5.960	5.928
3.62	— 3.55	6.520	6.46	6.58	6.601	6.586
3.22	— 2.55	7.141	7.165	7.142	7.189	7.210
2.82	— 1.55	7.728	7.838	7.682	7.764	7.815
2.42	— 0.55	8.295	8.431	8.227	8.323	8.380
2.02	0.45	8.839	8.993	8.735	8.852	8.922
1.62	1.45	9.350	9.564	9.311	9.340	9.413
1.22	2.45	9.798	9.995	9.763	9.769	9.839
0.82	3.45	0.183	0.285	0.174	0.117	0.190
0.42	4.45	0.502	0.480	0.521	0.452	0.478
0.02	5.45	0.749	0.533	0.622	0.660	0.680
9.62	6.45	0.943	0.601	0.687	0.850	0.836
9.22	7.45	1.148	1.132	1.389	1.084	1.026
8.82	8.45	1.317	1.20	1.607	1.248	1.102
8.42	9.45	(1.37)	(1.3)	(1.7)		(1.10)
8.02	10.45	(1.36)	(1.4)	(1.8)		(1.11)

The discussion of the densities must be deferred to a subsequent communication, because it will be necessary in that discussion to keep the stars of different galactic latitudes separated *ab initio*. There seems to be reason to believe that this discussion, if therein we include some additional data furnished by observation, will lead to a better understanding of the real structure of the galactic system.

The table 5 might therefore have been omitted here but for the fact that it brings out clearly a defect of our solution I and indicates at the same time the means to correct it. This defect lies in the rapid decrease of the density Δ for the larger parallaxes. A graphical

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representation in which the densities are taken for ordinates, while the abscissae are not the parallaxes, but the distances from the sun, shews the enormous rapidity of this decrease. Such a rapid decrease appears entirely incredible, as compared with the slow and gradual change for larger distances. If we could actually use stars which are evenly distributed over the whole sky, instead of almost exclusively over the northern hemisphere, and if the density varies continuously with the position in space, then the mean density in the immediate neighbourhood of the sun must even be found constant.

The values of Δ_2 show the same decrease. A variation of ϱ has thus no influence. The Δ_3's on the other hand show a still more rapid decrease. It follows immediately that by a *diminution* of ε the defect in question can be corrected. It appears from the Δ_4's that a change of the distances in the direction which is made necessary by CAMPBELL's results, has also an effect in the desired direction.

It is easily inferred from the table that the defect must nearly disappear by a new computation, if therein we determine the parallaxes in accordance with the value (13) of the sun's velocity, and adopt

$$\varepsilon = 0.87. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This alteration of ε is just inside the estimated limits of uncertainty of this quantity [1]).

The last column of table 5, which was computed with these data, shows that the density becomes indeed tolerably constant for all parallaxes larges than 0".01.

For this reason the solution V is the solution which in my opinion is to be preferred, though it remains possible that the subsequent discussion of the densities will necessitate further small changes in the values of the constants.

9. *Reliability of the results derived for the luminosity-curve.*

The values which were given to ϱ in solution II, and to ϱ and ε in solution III are outer limits, which were taken for the sake of the simplicity of the computations. With regard to ϱ the alteration is 9 to 10 times the p. e., for ε it exceeds nearly three times the estimated limit of uncertainty. Also the solution IV was made with values of the constants, the deviations of which from those of solution I probably exceed the real uncertainties of the latter.

Nevertheless the discrepancies between the different curves in table 6 are inconsiderable. It thus appears that the form of the curve is very little affected by errors in the constants of formula (1).

[1]) See Public. of the Astr. Lab. at Groningen No. 8, p. 10.

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Excepting the extreme ends of curve, which for evident reasons are rather uncertain, errors of 0.1 in the values resulting from solution V must already be considered as unprobable. In the middle of the curve this corresponds to only about 0.2 of a magnitude.

Besides on the uncertainties of the constants, the correctness of the curve also depends on the greater or smaller degree of completeness and certainty of the data about the magnitudes and the proper motions which form the basis of the whole investigation. We can however easily estimate the effect of these causes, as it is possible to derive the curve:

1st. exclusively from stars of app. mag. 3.1, 5.1, 7.1;
2nd. " " " " " " 4.1, 6.1, 8.1.

These two determinations are absolutely independent of each other. The computation was carried out with the data of solution I [1]), in precisely the same way as that for the last row of table 4, *i. e.* entirely independently of the densities. The results are given in the following table

M.	I Mag. 3.1, 5.1, 7.1	II Mag. 4.1, 6.1, 8.1	I—II
—6.55	4.730		
—5.55	5.183	5.272	—0.089
—4.55	5.957	5.930	+ .027
—3.55	6.638	6.561	+ .077
—2.55	7.229	7.233	— .004
—1.55	7.815	7.883	— .068
—0.55	8.349	8.454	— .105
0.45	8.875	9.013	— .138
1.45	9.368	9.482	— .114
2.45	9.821	9.927	— .106
3.45	0.222	0.280	
4.45	0.576	0.593	— .058
5.45	0.882	0.797	— .017
6.45	1.163	0.968	+ .085
7.45	1,291	1.165	+ .195
8.45	1.509	1.269	+ .126
9 45		1.390	+ .240

[1]) Afterwards this computation was also made for solution V. The results but identical to those of sol. I.

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Keeping in mind that we may legitimately expect that the errors in the adopted curve, so far as they depend on the uncertainties here considered, will range between limits only about half as wide as those of the differences I—II, we come to the conclusion that these differences are already very satisfactory. All things considered I think we may safely expect that (excepting the extreme ends of the curve) the values resulting from solution V will never be in error much more than 0.2, which corresponds to about 0.4 of a magnitude in the middle of the curve [1]).

Moreover our knowledge of the proper motions is increasing rapidly, so that we may reasonably hope that within a comparatively short time, we may be able to reduce still more the uncertainties of the curve.

Especially for the fainter end of the curve, which depends exclusively on the large proper motions of faint stars we will certainly soon have better data by which it can be corrected and continued.

From the above numbers the curve appears to reach a maximum about the absolute magnitude 10.5. Whether for fainter stars it will descend as rapidly or more rapidly, and whether it will soon reach a limit, below which no luminous stars exist, are questions to answer which a knowledge of the number of large proper motions of stars fainter than the ninth magnitude is required. It seems not at all impossible by the aid of photography to derive, even within a few years, an approximate knowledge of these proper motions for stars down to the 13th or even somewhat higher magnitudes.

At the brighter end the continuation will cause more difficulties, as it must depend on an accurate knowledge of the extremely *small* proper motions, which can only be slowly attained in the course of years.

A number of conclusions can at once be drawn from our results, which however I will defer till after the discussion of the densities. I will here only illustrate the meaning of the curve by a few numbers. According to the curve V, there will be in a space which contains

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[1]) The uncertainty resulting from errors in the adopted position of the Apex and in the corrections to Bradley's declinations, was left out of consideration here. I hope shortly to be able to give the alterations which result from these causes.

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2.000.000	stars			of the same luminosity as that of the sun						
1	star	with	100.000	times	greater	»	than	»	»	»
38	stars	»	10.000	»	»	»	»	»	»	»
1800	»	»	1.000	»	»	»	»	»	»	»
36000	»	»	100	»	»	»	»	»	»	»
440000	»	»	10	»	»	»	»	»	»	»
over 5000000	»	»	10	»	smaller	»	»	»	»	»
7500000	»	»	100	»	»	»	»	»	»	»

Below this degree of luminosity it seems that the number of stars ceases to increase. The first and last numbers are of course very uncertain.

It may also be remarked that we find a total density which is much larger than is commonly assumed.

The mean parallax of the stars of magnitude 5.3 becomes 0".0158 by the solution V. Inside a sphere with a radius corresponding to this parallax I find (by sol. V) already 43000 to 44000 stars whose luminosity is not smaller than $\frac{1}{15}$ of that of the sun. The number of the still fainter stars can not be determined. If on the other hand we adopt the usual approximation which assumes the same luminosity for all the stars, the number of stars inside the same sphere will of course be the number of stars of the apparent magnitude 5.3 and brighter. This number is (Potsdam system) only about 1730, that is only $\frac{1}{25}$ part of the number which was found above.

10. *Stars of the first and the second spectral type.*

Although the data relating to the separate spectral types are by far less certain than for all stars together, I will nevertheless mention the results which I derived from them, as they bear on the conclusions arrived at in a former paper.

The uncertainties are of two kinds:

1st. For Type I the constants (2) are very uncertainly determined.

2nd. Our knowledge of the spectra is far from so complete and accurate as could be wished.

For these reasons the following results, at least those for type I, do not deserve the same confidence as the preceding ones for all the stars together. With regard to the first point, it has already been mentioned that the total weight of the direct determinations of paral-

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lax, which were available for type I, is very small. It is not one sixth part of that for type II.

Moreover these parallaxes belong exclusively to bright stars of comparatively small proper motion. It would be of the highest importance for an investigation like the present, if observers, who devote themselves to the determination of parallaxes, would pay especial attention to the comparatively few stars of the first type with large proper motions.

As to the second point:

Having regard to the fact that the D.C. is only complete down to the stars of about the 6th magnitude, it is to be feared that of the fainter stars which it contains a larger number proportionally will belong to the photographically brighter stars of the 1st type than to the stars of the same (visual) magnitude of the second type. If this is so, our results will be systematically affected.

In order to get more certainty about this point I derived the ratio

$$P = \frac{\text{number of stars of Type II}}{\text{" " " " "} \quad I} \quad . \quad . \quad . \quad . \quad (16)$$

for different magnitudes, not only from PICKERING's data [1]) but also from the spectroscopic Dm (Decl. — 1° tot + 20°) of Potsdam [2]), which is complete down to the visual magnitude 7.5 and is thus of special value for our purpose.

PICKERING's results are given with the argument: photographic magnitude, while we require here visual magnitudes. The necessary data to effect this reduction are given in PICKERING's work; nevertheless the accuracy of the results is considerably impaired by this circumstance.

The result of my computations was:

Vis. mag.	Number stars in DC. Typ I.	Typ II.	P.	
3.50—4.00	74	52	0.70	
4.00—4.50	157	109	0.70	
4.50—5.00	301	234	0.78	
5.00—5.50	633	494	0.78	. . (17)
5.50—6.00	1348	1045	0.78	
(6.00—6.50	2717	2220	0.82)	

[1]) Annals of the Astrophys. Obs. of Harvard Coll. vol. 26, Part 1, p. 147.

[2]) Publ. des Astrophys. Obs. zu Potsdam 8er Bd. 3es Stück.

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The data for stars fainter than the 6th magnitude are included in brackets, because we cannot be sure that the two types are observed equally completely; there is even a strong probability to the contrary.

The Potsdam Dm gives a classification which differs from that of the D. C.

According to Harvard. Obs. 26, part I, p. 177 we have approximately:

$$\left.\begin{array}{l} \text{Class I of Vogel} = A + F + G \text{ Draper Cat.} \\ \text{„ II „ „} = K \text{ „ „} \end{array}\right\} \quad \ldots . \quad (18)$$

Now I find by countings in the Potsdam Dm.:

mag. BD,	Cl. I.		Cl. II.		$\frac{\text{Cl. II}}{\text{Cl. I}}$		
0—3.5	40		10		0.25		
3.6—4.0	19	86	16	40	0.84	0.47	
3.1—4.5	27		14		0.52		
4.6—5.0	44		39		0.89		
5.1—5.5	68	276	39	151	0.58	0.55	
5.6—6.0	164		73		0.44⁵		
6.1—6.5	300		185		0.62		(19)
6.6—7.0	552	1708	308	953	0 56	0.56	
7.1—7.5	856		460		0.54		
7.6—8.1	66		35		0.53		
8.1—8.5	38	113	16	57	0.43	0.50	
8.6—9.0	9		6		0.67		

It follows from these numbers that, at least down to the visual magnitude 7.5 the quotient $\frac{\text{Cl II}}{\text{Cl I}}$ does not sensibly vary with the magnitude.

Accordingly we have by (17) in the notation of the D. C.

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$$\frac{K}{A+F+G} = \text{Const.} = \beta$$

from which

$$\frac{K+F+G}{A} = \frac{\text{Type II}}{\text{Type I}} = P = \beta + (\beta+1)\frac{F+G}{A}. \quad . \quad (20)$$

From the data of the D. C. reduced to visual magnitudes I find

vis. mag.	Number $F+G$	Number A	$\frac{F+G}{A}$
3.5—4.0	21	63	0.34
4.0—4.5	44	134	0.33
4.5—5.0	94	255	0.37
5.0—5.5	200	560	0.36^5
5.5—6.0	425	1269	0.33^5
6.0—6 5	908	2629	0.34^5

Thus also the last term of (20) appears to be eminently constant.

From the Potsdam Dm we thus derive the conclusion, which is in good agreement with the directly derived table (17), that the value of P does not sensibly vary with the magnitude (at least not down to mag. 7.5).

The numbers of stars of the two types were now derived as follows, the very few stars brighter than 2.5 being omitted:

1st. *Magnitudes* 2.5—3.5. All stars of these magnitudes in the whole of the sky were brought together, as explained above.

2nd. *Magnitudes* 3.5—6.5. The spectra of the Bradley stars [1]) were taken from the D.C. and the whole of the stars which are in this catalogue were counted between the same limits of proper motion and photometric magnitude as in table 1. From these countings the total number of these stars for the whole of the sky was then derived in the manner which has been explained above. Finally the numbers of stars of the different magnitudes (2.5—6.5) were multiplied by such factors (differing little from unity) that the con-

[1]) The stars which have been excluded have already been mentioned above.

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dition $P = \text{const.}$ is fulfilled, while the total numbers (Type I + Type II) are left unchanged.

3rd. *Magnitudes* 6.5—7.5. To begin with the same method was used for these stars as for those of the magnitudes 3.5—6.5. The number of stars in Bradley belonging to these magnitudes is so small however, that the numbers for the individual proper motions necessarily run somewhat irregularly. Therefore I first divided the whole of the stars in two parts, *viz.* those with proper motions $< 0''.10$ and those with proper motions $> 0''.10$.

The ratio $a = \frac{\text{number of stars of 1st Type}}{\text{id. 1st Type + 2nd Type}}$ was then determined

separately for each of these parts and compared with the analogous ratio for the magnitude 6.1. It appeared that the factors, by which these ratios for the magnitude 6.1 must be multiplied to give those for the magnitude 7.1, were very near unity. These factors were then used to derive the ratios a for the *separate* proper motions $0''.00—0''.01$,, $0''.01—0''.02$ ... etc. for the magnitude 7.1. Once these ratios a found, the table 1 furnishes the necessary numerical values.

In this way I found finally the numbers which are given in the following table: (p. 685)

It appears from this table that the numbers for type I show still considerable irregularities, which are still more apparent, if the table is condensed by taking wider limits of proper motion, and if then all the numbers are expressed as fractions of the analogous numbers of table 1. It appears in this way that *e. g.* the number of stars of large proper motion of the magnitude 5.1 is considerably smaller than might be expected from the same numbers for the magnitudes 4.1 and 6.1. At first sight such an irregularity is rather surprising, as it is not at once apparent how the spectrographic observations can be subject to systematic errors depending on the proper motion.

A closer scrutiny shows however that such a thing is not at all impossible in the present case.

In Astronomy and Astrophysics Vol. XII, p. 811 are given a number of corrections to the data of the D. C., which corrections I have duly applied.

The corrections bear exclusively on stars of large proper motion, whose spectrum has been reinvestigated on the indication of Mr. W. H. S. Monck. In how far these corrections influence the number of stars of the first type with large proper motions is apparent from the preceding

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TABLE 7. Number of stars in the whole sky.

	TYPE I.					TYPE II.				
μ	3.1	4.1	5.1	6.1	7.1	3.1	4.1	5.1	6.1	7.1
0″.000— 0″.009	2	15	76	220	914	3	8	17	121	590
.010— .019	8	37	128	435	1227	7	16	68	199	669
.020— .029	8	28	126	332	1007	1	14	54	262	903
.030— .039	9	20	117	345	1154	7	7	73	194	756
.040— .049	7	19	47	284	872	5	8	45	174	618
.050— .059	8	18	53	201	665	5	5	34	155	584
.060— .069	2	18	50	130	470	2	7	28	121	493
.070— .079		13	24	112	320	2	6	46	136	432
.080— .089	2	12	21	112	349	3	13	24	97	343
.090— .099	6	10	19	66	199	2	7	34	136	447
.100— .149	4	24	62	173	391	6	32	88	253	572
.150— .199	6	8	21(2)	51	117	2	24	56	132	303
.200— .299	3	10(3)	5(12)	19(19)	29	9	22	65	185	286
.300— .399	1	2	2(4)	(5)		2	14	39	107	75
.400— .499	2		2	5	17	3	11	15	30	104
.500— .599						3	8	7	24	38
.600— .699				(5)			2	7	5	24
.700 — .799							8	5	10	17
.800— .899							3	2		12
0.900— 0.999								2		6
1.000— 1.199						1	3	5		7.5
1.200— 1.399							3	2	5	12.0
1.400— 1.599								2		4.5
1.600— 1.799										1.5
1.800— 1.999							2	2		1.5
2.000— 2.999						1				6.0
3.000— 3 999									5	3.0
4.000— 4.999								2		1.5
5.000— 5.999									5	
6.000— 6.999										1.5
7.000— 7.999										
	68	234	753	2435	7731	64	223	722	2356	7311

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table. If the corrections had been neglected, the numbers of stars of the magnitudes 4.1, 5.1, and 6.1 would have been increased by the quantities which are added in brackets.

For the magnitude 7.1 the analogous increase could not easily be derived, owing to the particular manner in which the numbers for that magnitude were obtained. It will be seen that by these corrections the proportions are entirely changed in the case of the very large proper motions of type I [1]).

If the corrections which are still necessary are so considerable, we cannot expect very reliable results.

The manner in which I tried as completely as possible to remove the irregularities, will best be shown by an example: The total numbers of stars of type I for the magnitudes 4.1, 5.1 and 6,1 are 234, 753 and 2485. If now every number of the third column is multiplied by $\frac{753}{234}$, and every number of the fifth column by $\frac{753}{2485}$, these three columns are reduced to the same total number.

After this was done the numbers of the 3rd, 4th and 5th columns were added; the sums were divided by 3 and the resulting values were adopted as corrected values for the magnitude 5.1. In the same way the corrected numbers for the magnitudes 4.1 and 6.1 were derived. In order to be able to do the same for mag. 3.1 the numbers for mag. 2.1 were also derived. The numbers for mag. 7.1 were not altered.

In the case of type II the number of large proper motions is so considerable, and the influence of the corrections which have just been discussed is so small, that the numbers of table 7 were adopted as they stand.

In order to derive from table 7 (altered for type I as just now explained) the densities and the luminosity-curve in the same way as explained above, a first computation was made with the values (2). Afterwards a second computation was carried through in which the corrected value (15) of ε was used and the parallaxes were made to agree with the corrected velocity (13) of the solar system.

In the case of type I the alteration of ε had a large influence on the value of $\pi_{5.5}$ derived from the directly measured parallaxes, owing to the fact that these direct determinations belong exclusively to very bright stars.

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[1]) According to Mr Monck 60 percent of the stars of type I, to which he called attention on account of their large proper motions, were actually altered to type II.

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The following are the values of the constants for the two solutions (A and B):

Type	Sol.	k	A	p	ϵ	ρ	
I	A	16.7	0.116	1.11	0 905	0.19	(21)
"	B	18.45	0.0753	1.20	0.87	0.19	
II	A	16.7	0.0262	1.54	0.905	0.19	
"	B	18.45	0.0316	1.47	0.87	0.19	

With these data the following densities were found:

TABLE 8. Densities Δ.

π		Type I.				Type II.			
Limits.	Mean.	Sol. A		Sol. B		Sol. A		Sol. B	
0″00100 — 0″00158	0″00118	0.280		0.278		0.070		0.102	
.00158 — .00251	.00187	.470		0.478		0.156		0.190	
.00251 — .00398	.00296	.738		0.726		0.254		0.314	
.00398 — .00631	.00469	1.006		0.986		0.440		0.474	
.00631 — .0100	.00743	1.202		1.172		0.622		0.655	
.0100 — .0158	.0118	1.215		1.171		0.802		0.790	
.0158 — .0251	.0187	1.189		1.283		0.960		0.933	
.0251 — .0398	.0296	1.000		1.000		1.000		1.000	
.0398 — .0631	.0469	0.822		0.826		0.993		1.186	
.0631 — .100	.0743	0.669		0.669		0.940		1.083	
.100 — .158	.118	0.338	0.583	0.505	0.619	0.883	0.908	1.059	1.072
> 0.158	.204	0.290		0.368		0.598		0.981	

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For the luminosity-curve we find:

TABLE 9. Luminosity-Curve.

(Log. number per unit of volume for $\pi = 0''.0296$)

Log. L.	M.	Type I		Type II	
		Sol. A -0.039	Sol. B	Sol. A -0.078	Sol. B
4.82	—6.55	4.433	4.382	4.182	4.192
4.42	—5.55	4 951	5 000	4.702	4.678
4.02	—4.55	5.640	5.636	5.375	5.371
3.62	—3.55	6.223	6.262	6.104	6.131
3.22	—2.55	6.804	6.854	6.767	6.849
2.82	—1.55	7.358	7.422	7.443	7.491
2.42	—0.55	7.902	7.972	8.046	8.116
2.02	0.45	8.413	8.477	8.634	8.703
1.62	1.45	8.902	8.907	9.170	9.232
1.22	2.45	9.308	9.362	9.635	9.691
0.82	3.45	9.644	9.632	0.062	0.054
0.42	4.45	9.927	9.843	0.401	0.422
0.02	5.45	0.093	0.002	0.670	0.640
9.62	6.45	0.297	0.139	0.937	0.818
9.22	7.45	(0.50)	(0.08)	1.080	1.004
8.82	8.45			1.306	1.115

In table 8, Sol. A. we again find, for both types, a strong decrease of the density with diminishing distance. By the alteration of ε to 0.87 and the slight alteration to the distances in Sol. B. this decrease disappears practically entirely for type II. For type I the decrease has become somewhat less rapid, but it has not disappeared. The weight of this result is but very small however. The number of stars of type I whose parallax is $> 0''.063$, is so small that any conclusion based thereon is of necessity little reliable, especially in a case like the present where, as has been shown above, the adopted number of stars with large proper motions may be very materially in error. For reasons which have already been mentioned, it must be considered as probable that, as soon as more reliable data will be available, we will, for this type also, find the density not far from constant for parallaxes larger than $0''.02$.

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As a consequence of this result some of the conclusions, at which I had previously arrived (Proceedings Jan. 1893), must be withdrawn, or at least considerably altered.

These conclusions were based on the result, derived by STUMPE, RISTENPART, and others, *viz.* that, if the stars are arranged in groups according to their proper motions, the mean parallaxes of these groups are approximately proportional to the mean proper motions. It is only subsequently that I found that this result was arrived at by an illegitimate reasoning and is certainly not in accordance with the facts.

For the stars with *large proper motions* (say larger than 0".10) it follows from the above that the variation of the quantity Q in the paper quoted, is, either entirely or at least to a large extent, a consequence, not of a condensation of the stars of type II in the neighbourhood of the sun, but of the fact that the number of faint stars of the first spectral type, as compared to the number of bright stars of the same type, is not so large as in the case of the second type.

Physiology. — H. D. BEYERMAN: "*On the influence upon respiration of the faradic stimulation of nerve tracts passing through the internal capsula.*" (Communicated by Prof. C. WINKLER).

In a recent publication WINKLER and WIARDI BECKMAN [1]), in stimulating with the faradic current the lateral part of the praecrucial circumvolution in a dog's brain, have proved the influence of this field of the cortex upon the respiratory movements. Acceleration of rhythm and an inspiratory position of the thorax were the effects generally obtained during the faradisation of this spot (fig. 1, compare the fields 11, 12, 15 and 16).

Repeating their experiments I found, that faradisation of the most proximal parts of the above mentioned spot (the fields 15 and 16) causes only acceleration of rhythm (or if respiration is very frequent, increase of the amplitude of each respiration), whereas faradisation of its caudal part (the fields 11 and 12) is followed by a forced inspiratory position of the thorax.

Hence there are to be adopted, two cortical spots regulating the respiration, one, proximal, accelerating rhythm, the other caudal, forcing the inspiration. Both are situated on the lateral end of the praecrucial circumvolution.

[1] WINKLER and WIARDI BECKMANN. Proceedings Vol. I, 25 March 1899.

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In repeating the experiments of SPENCER [1]) I succeeded to define the traject of the efferent fibres from the two above mentioned centra through the corona radiata and the capsula interna.

Forced inspiratory position of the thorax is always obtained, during the faradisation of a distinct spot situated, in horizontal sections through the brain (fig. 4 and fig. 6 in +), about the middle of the corona radiata and of the capsula interna. In frontal sections it was found (fig. 9 in +) in the pes pedunculi (curves fig. 5, 8 and 10).

The central traject of the pyramidal tract is stimulated in these experiments, and even if the hemispheres are totally removed, forced inspiration (accompanied by stretching of the neck, by lifting up the tail, and by ejecting urine in a jet) still follows during the stimulation of this tract.

Acceleration of rhythm is always caused by faradisation of a distinct spot, situated in horizontal sections through the corona radiata and through the higher level of the capsula interna (fig. 4 and fig. 6 in 0) proximal to the former, close to the foremost part of the caput nuclei caudati.

In frontal sections this spot is found (fig. 9 in 0) on the latero ventral face of the nucleus caudatus, and dorsal in respect to the former spot (to compare curves in fig. 5, 7, 8 and 10).

Therefore this nerve tract, by which the acceleration of rhythm is conducted, runs through the proximal part of the corona radiata, in the foremost part of the internal capsule, proximal to its knee, close to the antero- and ventral face of the nucleus caudatus.

Perhaps this nerve tract may find a preliminary end in the basal ganglia, but my efforts in following its traject through them are not crowned by a positive result. SPENCER followed it until a region in the vicinity of the grey surroundings of the third ventricle, where it perhaps could be identified with the centrum of acceleration of rhythm, mentioned by CHRISTIANI.

In horizontal sections, cutting through the capsula interna, two more spots, (fig. 6 on △ and ▭) are found, the influence of which upon respiration may be demonstrated by faradisation. The more proximal one answers to faradisation with a slight retardation of rhythm, whereas the faradisation of the caudal part, reaching as far as the white layer round the cornu Ammoni, sets a very intense inhibition. The respiration is retarded, or may be even stopped in an expiratory position of the thorax.

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[1]) SPENCER. Phil. Transactions. Vol. 185, p. 609

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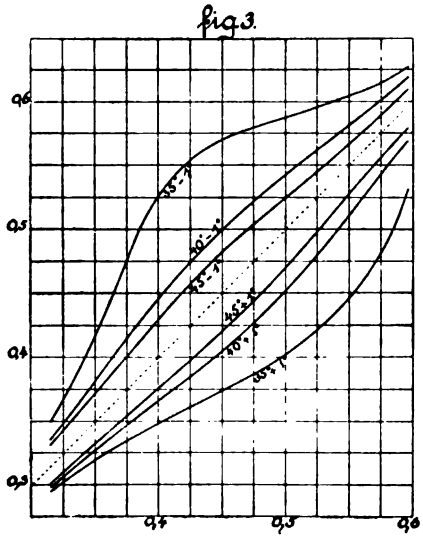
Physics. — Dr. H. KAMERLINGH ONNES: "*On differences of density in the neighbourhood of the critical state arising from differences of temperature.*" (Appendix to Communication N°. 68 from the Physical Laboratory at Leiden).

§ 1. At the former meeting I have demonstrated (Communication N°. 68) that the deviations from VAN DER WAALS' theory mentioned by DE HEEN, are not to be found when his experiments are repeated with pure carbon dioxide. From which I derived that systematical corrections must be applied to his results. Moreover I have proved experimentally that DE HEEN has wrongly left out of consideration differences of temperature resulting from adiabatic processes.

Other and perhaps very important differences of temperature may have arisen from DE HEEN's method of heating, as I briefly mentioned in § 3. As long as there are no proofs to the contrary we must consider that they have really existed. If other sources of errors could not be undoubtedly demonstrated, as has been done in Communication N°. 68, and if not small differences of pressure, which may have remained, might have had a similar influence as the differences of temperature meant here, we would be fully justified in ascribing entirely to them the deviations found by DE HEEN. For in the different experiments these deviations are related in a manner such as we should expect if the temperature in the upper part of the apparatus was higher than in the lower part, in agreement with the supposition laid down in § 2 l. c. It seemed to me desirable to explain here more in detail that this was the case, especially because with other experiments on the critical state, attention must be paid to deviations of the same kind, even when they are reduced to much smaller dimensions by the precautions of the observer.



From AMAGAT's observations in the neighbourhood of the critical state plotted in a diagram with regard to density and pressure the densities at intermediate temperatures are easily found by interpolation with the coefficients of pressure. In fig. 3 at ∂_t (the density at the temperature t) as abscissa I have plotted as ordinates ∂ itself and also ∂_{t+1} and ∂_{t-1},

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the values which under the same pressure are related to temperatures which are situated either 1 deg. C. higher or 1 deg. C. lower than t. The isothermal of density ∂_t gives in this figure the same line for all values of t (it is drawn as a dotted line at an angle of 45°). Two curves ∂_{t+1} and ∂_{t-1} belong to each temperature t and indicate by the difference of their ordinates from that of the line drawn at an angle of 45° the variation of density for 1 deg. C. difference of temperature from the density ∂_t at $t°$. In this way the deviations for 1 deg. C. at 35° C., 40° C. and 45° C. are each represented by two of these curves of deviation.

This figure shows very clearly that at some densities even small differences in temperature at 35° C. may lead to important variations in density. For the correction to the experiments treated in Communication N°. 68 § 2 it gives much larger values, than those derived there by means of a mean coefficient of expansion. The latter had wrongly been calculated from the difference in density between two limits of temperatures within which the coefficient of density variation has a maximum. The use of a mean coefficient of expansion is only allowed within narrow limits of temperature in that case. However in judging DE HEEN's experiments, I have attached small value to this correction. The measurement of the difference of temperature, from which it must be calculated, left much to be desired in my preliminary determinations; (the reason why further determinations were not made has been explained in § 1 of Communication 68). During the experiments one of the wires of the thermo-element was broken, so that a correction must be applied to the differences of temperature measured. This is not of any account for the measurement of the variation of the difference in temperature (Comp. § 3) of the two reservoirs caused by the opening of the cock, but yet leaves uncertain this difference in temperature itself. And the chief arguments for the refutation of DE HEEN's hypothesis was that I found the densities in the upper reservoir only slightly smaller than those in the lower, although it was certain that the former had a somewhat higher temperature than the latter.

§ 2. With very small differences of temperature the difference of the mean densities in two parts of a cylinder in which the temperature varies with the height according to a given law (e.g. linearly) can easily be calculated. In a case such as the experiments of DE HEEN it seems to me probable that we may put:

$$t = t_0 + 2\lambda h,$$

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in which t_0 stands for the temperature at a given height, for instance that of the cock of his apparatus, and h for the height of the layer with temperature t, above that given height.

If ∂_{pt} represents the density at a given pressure and temperature then we may put, at very small differences of temperature

$$\partial_{pt} = \partial_{pt_0} + \Delta\,(t - t_0),$$

in which $\Delta = \frac{d\partial_p}{dt}$ can be deduced from fig. 3. If the upper end of the upper reservoir stands at h_s and the lower end of the lower reservoir at h_i, then the mean density ∂_s in the upper reservoir and ∂_i in the lower reservoir is:

$$\left.\begin{aligned} \partial_s &= \partial_{pt_0} + \Delta\,\lambda\,h_s \\ \partial_i &= \partial_{pt_0} + \Delta\,\lambda\,h_i \end{aligned}\right\} \quad \ldots\ldots\ldots (1)$$

In the case of DE HEEN, putting $h_s - h_i = 1$, λ gives the difference between the temperature at the middle of the upper and of the lower reservoirs.

For the mean density ∂_m in the whole reservoir from

$$\partial_s h_s - \partial_i h_i = \partial_m$$

we find

$$\partial_m = \partial_{pt_0} + \Delta\,\lambda\,(h_s + h_i). \quad \ldots\ldots\ldots (2)$$

In DE HEEN's first series of experiments, neglecting the dimensions of the cock we find

$$h_s = 0{,}5 \quad h_i = -0{,}5 \quad \partial_m = \partial_{pt_0}$$

and so what DE HEEN gives in this series as the densities of vapour ∂_{dI} and of liquid ∂_{vI} we find to be

$$\left.\begin{aligned} \partial_{dI} &= \partial_m + 0{,}5\,\Delta\,\lambda \\ \partial_{vI} &= \partial_m - 0{,}5\,\Delta\,\lambda \end{aligned}\right\} \quad \ldots\ldots\ldots (3)$$

and the difference of the so-called vapour and liquid density at the same ∂_m

$$\partial_{vI} - \partial_{dI} = -\Delta\,\lambda. \quad \ldots\ldots\ldots (3^a)$$

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In DE HEEN's second series of experiments a difference must be made between a determination of what he calls a vapour density and what he calls a liquid density. (Comp. Communication N°. 68).

In the first case we must put $h_s = 0{,}229$, $h_i = -0{,}771$ and according to (2)

$$\partial_m^{(d)} = \partial_{t_0}^{(d)} + \Delta\lambda\,(0{,}229 - 0{,}771)$$

in the second case

$$\partial_m^{(v)} = \partial_{t_0}^{(v)} + \Delta\lambda\,(0{,}845 - 0{,}155).$$

So that by means of (1) we find for the vapour density ∂_{dII} and the liquid density ∂_{vII} given by DE HEEN in the series

$$\left.\begin{aligned} \partial_{dII} &= \partial_m^{(d)} + 0{,}771\,\Delta\lambda \\ \partial_{vII} &= \partial_m^{(v)} - 0{,}845\,\Delta\lambda \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4)$$

or also for the same value of $\partial_m^{(d)}$ and $\partial_m^{(v)}$

$$\partial_{vII} - \partial_{dII} = -1{,}62\,\Delta\lambda. \quad \ldots\ldots\ldots \quad (4^a)$$

In the two series the same value will have to be put for λ, and Δ will also be the same at the same ∂; hence it follows from (3^a) and (4^a) that the deviations, which originate in λ, will be much greater in the second series than in the first.

DE HEEN found for the experiment treated in Communication N°. 68, § 2 and § 3 in the first series

$$\partial_{vI} - \partial_{dI} = 0{,}088$$

in the second series, where another source of error occurred (comp. Communication N°. 68).

$$\partial_{vII} - \partial_{dII} = 0{,}190.$$

From the combined deviations at 35°, 40° and 45° C. in DE HEEN's second series according to the table considered in Communication N°. 68, if we desired to attribute the deviations found *exclusively* to the differences in temperature considered now and if we equalise λ for all temperatures, I find $\lambda = 1°{,}35$. Here I have put the deviation for 1 deg. increase for Δ in the ∂_d equation, that for 1 deg. decrease in the ∂_v equation, both derived from fig. 3.

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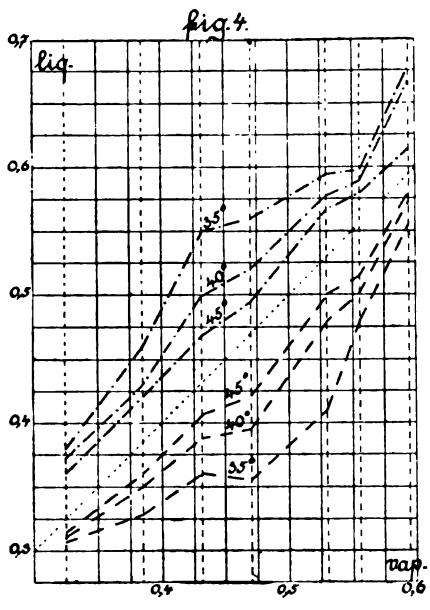
Then approximately we have

$$\partial_{d\,II} = \partial_m^{(d)} + \Delta$$

$$\partial_{v\,II} = \partial_m^{(v)} - \Delta$$

The so-called liquid densities and vapour densities of this series of DE HEEN (as in § 4 of Communication N°. 68) if drawn as ordinates against the mean-density as abscissa, must then give the same figure as fig. 3. From fig. 4 may be seen that this is actually the case. This figure gives the curves for 35° C., 40° C. and 45° C. for DE HEEN's experiments borrowed from a drawing by VERSCHAFFELT (comp. Communication N°. 68). Except for accidental errors the figure is in sufficient agreement with fig. 3. The whole system of deviations from DE HEEN's experiments agrees therefore with that which would result from the supposed distribution of temperature.



§ 3. Also the increase of the vapour density with regard to the mean density in DE HEEN's experiments below the critical temperature (see fig. 1 of Communication N°. 68) is in correspondence with the supposition that the temperature increases in the direction from the lower reservoir to the upper. In fig. 2 of the same, calculated from AMAGAT's observations supposing that in the two reservoirs of DE HEEN the temperature was everywhere the same, this rise of the curve on the vapour side, as long as the liquid surface does not enter into the upper reservoir, does not of course occur. If however the temperature in the two reservoirs increases in the said direction the temperature at the height of the liquid surface in the lower reservoir will be higher at a greater than at a smaller mean density. The maximum vapour tension increases therefore and also the density in the upper reservoir. This will be even more the case with temperatures coming nearer to the critical than with lower temperatures. This peculiarity is also found in the deviations of DE HEEN's results.

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Mathematics. — Prof. J. DE VRIES: "*Involutions on a curve of order four with triple point.*"

1. If the points of a plane curve of order four, C_4, having in O a triple point, are arranged into the pairs P_1, P_2 of a quadratic involution, I_2, the right lines $P_1 P_2$ envelop a curve, Γ^3, of the third class (envelope of involution).

For, through O no other tangents of the envelope of involution can pass than the right lines connecting the points of contact O', O'', O''' of the three tangents of C_4 in O with the points conjugate to them in I_2.

The tangents from any point M to Γ^3 evidently contain the three pairs of points which I_2 has in common with the biquadratic involution, the groups of which are determined by the rays through M.

Let us now consider two pairs P_1, P_2 and Q_1, Q_2 of I_2 and a point S' of C_4. The pencils of conics having as basepoints O, S', P_1, P_2, and O, S', Q_1, Q_2 intersect C_4 in the pairs of two new quadratic involutions having one pair S'', S''' in common. The involution I_2, completely determined by the pairs P_1, P_2 and Q_1, Q_2, can be generated by means of the pencil of conics with the basepoints O, S', S'', S'''. So:

Each quadratic involution can be generated by means of an infinity of pencils of conics whose variable basepoints form a cubic involution.

The degenerated conics of the pencil ($O\,S'\,S''\,S'''$) furnish three pairs of I_2, lying on the sides of the triangle $S'\,S''\,S'''$. Each pair A_1, A_2 of I_2 lies in a right line with a pair T', T'' of the "conjugate" I_3; for, if the conic connecting any pair of I_2 with O, T', T'', intersects C_4 still in T''', then O, T', T'', T''' are the basepoints of a pencil generating I_2. So:

The two conjugate involutions I_2 *and* I_3 *have the same envelope of involution* Γ^3.

2. Of the tangents from Γ^3, passing through the point P_1 S' of C_4, one bears the point P_2 conjugate to P_1 in I_2; the other two tangents connect S' with the points S'' and S'', forming with S' a group of I_3.

If V' is a branchpoint of I_3, the corresponding points V'' and V''' coincide; their connecting line is a common tangent of C_4 and Γ^3, V' lying on Γ^3, because the right lines $V'\,V''$ and $V'\,V'''$ are coincident.

If the right line $S'\,S''$ coincides with the right line containing P_1 S' and P_2, then P_1 and P_2 take the place of the pair Q_1, Q_2 of I_2 lying

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on S' S''. So this case can present itself only when Q_1 coincides with S', so that the curves C_4 and Γ^3 touch each other in S'. The number of those points of contact corresponds to the number of coincidences of the correspondence which arises when two points Q_1 and S' lying on the same tangent of Γ^3 are made to correspond to each other. Each point S' indicating two pairs Q_1, Q_2 whilst each pair Q_1, Q_2 furnishes a pair S', S'', the correspondence has the symbol (2, 4). So C_4 and Γ^3 touch each other in six points R.

So the 18 common tangents of C_4 and Γ^3 are represented by the 6 tangents in the points R counted double and by the right lines forming the 6 coincidences of I_2 and I_3.

Each point R takes the place of two points of intersection of C_4 and Γ^3; these curves having moreover still the branchpoints of I_3 in common; the envelope of involution Γ^3 is a curve of order four, thus of deficiency zero. The double tangent of Γ^3 contains the two pairs common to I_2 and I_3 or, what comes to the same, two pairs of I_2.

3. If the points O' and O'' form a pair of I_2, the envelope Γ^3 breaks up into a conic of involution Γ^2 and the point O.

Now the pairs of the points S', S'', in which C_4 is intersected by the right lines P_1 P_2, form a second quadratic involution J_2. For, one of the tangents out of $P_1 \equiv U'$ contains the point P_2, whilst the other bears a pair Q_1, Q_2 of I_2 and the point U'' conjugate to U'.

Evidently the "conjugate" involutions I_2 and J_2 have the pair O', O'' in common. The tangents from O to Γ^2 connect O''' with the points conjugate to O''' in I_2 and J_2.

The right line bearing the pair A_1, A_2 of I_2 and the pair B_1, B_2 of J_2 can become a tangent of C_4 in two different ways. First, when A_1 coincides with A_2 or B' which B''; the coincidences of the two involutions furnish four common tangents of Γ^2 and C_4. Secondly when A_1 coincides with B'; then this gives rise to a point of contact of Γ^2 and C_4. As C_4 is of the sixth class, there will be four suchlike points of contact; indeed, this also ensues from the fact, that between the points A_1 and B' exists a correspondence (2,2). So:

The conics of involution Γ^2 touch C_4 four times.

The conic Γ^2 is determined by one of its points of contact R; for of I_2 and J_2 we then know two pairs, namely O', and O'' and the pair consisting of R and one of its tangential points.

The points of contact of the envelopes Γ^2 form a biquadratic involution given at the same time with C_4, which can therefore be called a *fundamental involution*.

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The points O', O'', O''' forming three pairs there are three fundamental involutions and three systems of conics touching four times.

The conjugate I_3 being broken up into J_2 and the point O, the pairs of I_2 lie in conics through two points B', B'' of J_2, touching in O a fixed right line, which forms with B' B'' a conic of the indicated pencil; so it has in O four points in common with C_4 and is therefore the tangent t''' in O'''.

Each pair of I_2 can be connected with each pair of J_2 by a conic touched by t''' in O.

4. If B' and B'' coincide in a point D_I, the corresponding pencil contains two envelopes touching C_4 still in a second point D_{II}.

The quadratic involution I_2 determined by the pairs O', O'' and D_I, D_{II} evidently coincides with its conjugate J_2; for, J_2 contains the same two pairs. The tangents drawn from any point of C_4 to Γ^2 connecting this point with the two points with which it forms pairs of I_2 and J_2, the envelope Γ^2 will in this case degenerate into a point Δ to be counted double.

Each ray through Δ bears two pairs of I_2 conjugate to itself. Two tangents from Δ to C_4 contain each a coincidence of the involution; the remaining four are represented by two double tangents, taking together the place of the conic belonging to I_2 and touching C_4 four times.

The second point D_{II} belonging to D_I determines in the same way a similar particular I_2, of which the point of contact, counted double, of the remaining two double tangents is to be regarded as Γ^2. So:

Each of the six points of intersection of the double tangents is the centre of a pencil of rays, each ray of which bears two pairs of a fundamental involution [1]).

We may suppose that the notation for the double tangents d_1, d_2, d_3, d_4 has been chosen in such a way that the points $\Delta_{12} \equiv d_1 d_2$ and $\Delta_{34} \equiv d_3 d_4$ belong to the fundamental involutions having the pair O', O'' in common, Δ_{13}, Δ_{24} being in likeway conjugate to O', O''' and Δ_{14}, Δ_{23} to O'', O'''.

The right lines connecting a point D_I of C_4 with Δ_{12} and Δ_{34}

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[1]) These fundamental involutions present themselves also on a C_4 with three nodes (comp. J. DE VRIES, *La quartique trinodale*, Archives Teyler, t VII, § 16). Also a C_4 with two nodes contains similar involutions (comp. J. DE VRIES, *Over vlakke kromme lijnen van de vierde orde met twee dubbelpunten*, Nieuw Archief voor Wiskunde, vol. XIV, 1888, p. 197.)

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contain respectively the points D_{II} and D'', conjugate to D_I in the corresponding fundamental involution. Now it is easy to see that the right lines $\Delta_{12}\ D''$ and $\Delta_{34}\ D_{II}$ intersect each other in a point D' of C_4.

For, if we determine an involution I_2 by the pair O', O^* and the double point D_I, then D_{II} and D^* are the double points of the conjugate J_2. In the second double point D' of I_2 the curve C_4 touches a conic, touching it moreover in D^* (D_{II}) and in O'''; consequently D', D^* and D', D_{II} are pairs of the indicated fundamental involutions. So:

Any two opposite vertices of the quadrilateral formed by the double tangents are therefore two adjoined vertices of an infinite number of quadrangles described in C_4 [1]).

An involution I_2 being projected from O by an involution of rays, the theorem holds good: "The pairs of rays projecting from O the points of contact of two double tangents, lie in involution with a pair of tangents in O and with a pair formed by the third tangent in O and the ray through the point of intersection of the double tangents."

5. The cubic involution conjugate to a quadratic (§ 1) is not the most general one. One of its groups contains the points O', O'', O''', so that its envelope of involution consists of Γ^3 and the point O to be counted three times.

The general I_3 has an envelope of involution of the sixth class: the six tangents through O connect respectively O', O'', O''' with the two points conjugate to them.

We shall consider the two groups A_1, A_2, A_3 and B_1, B_2, B_3. The pencils of conics having as basepoints $(O\,A_1\,A_2\,A_3)$ and $(O\,B_1\,B_2\,B_3)$ intersect C_4 in two quadratic involutions. Let P', P'' be the common pair of points and Q the fourth point of intersection, not situated on C_4, of the conics $(O\,P'\,P''\,A_1\,A_2\,A_3)$ and $(O\,P'\,P''\,B_1\,B_2\,B_3)$, then I_3 can be generated by means of the conics of the pencil $(O\,P'\,P''\,Q)$. So:

Each cubic involution can be determined by a pencil of conics.

Each of the degenerated conics $(O\,P', Q\,P'')$ and $(O\,P'', Q\,P')$ furnishes a linear group, that is, a group the three points of which lie in a right line.

So the envelope Γ^6 has two triple tangents.

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[1]) Comp. § 15 of the previously mentioned paper: „La quartique trinodale".

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It also possesses double tangents. The points S and S' lying in a right line with a pair of I_3 are conjugate to each other in a correspondence (4, 4). For, two of the tangents out of $S \equiv P_1$ to Γ_6 connect P_1 with P_2 and P_3; each of the remaining four contains a pair of I_3 as well as a point S'. The system (S, S') has eight pairs in common with I_3; so there are 4 right lines, each bearing two pairs of I_3; that is, Γ^6 possesses four double tangents; so it is of deficiency *zero* and of order *ten*.

To every point S eight points P, to every point P 4 points S correspond. In each of the 12 coincidences R of the system (S, P) the curves C^6_4 and Γ^6_{10} touch each other. The remaining 12 common tangents originate from the 4 coincidences of I_3 and the 8 coincidences of the system (S, S').

Besides the 12 points of contact R, the curves C^6_4 and Γ^6_{10} have still 16 points in common, four of which belong to the double points of I_3 as branchpoints; the remaining twelve are points of S for which two points S' coincide.

6. When O', O'' form a pair of I_3 the envelope of involution breaks up into a point O and an envelope Γ^5.

An involution I_3 is fully determined by a triplet A_1, A_2, A_3 and two pairs B_1, B_2 and O', O''. The conic through A_1, A_2, A_3 touching C_4 in O''' intersects it still in a point P. Through B_1, B_2 and P we draw a second conic touching C_4 in O'''; it has with the first another point, not situated on C_4, in common. The pencil $(O''' O''' P Q)$ contains the conic $(O''' P, O''' Q)$ determining on C_4 a triplet of points, two of which coincide with O' and O''. So the involution I_3 in which C_4 is intersected by this pencil contains the triplet A_1, A_2, A_3 and the pairs B_1, B_2 and O', O''; so it is identical with the given involution.

The right line PQ bears a linear group and is therefore a triple tangent of Γ^5. The system (S, S') being now qualified by the symbol (3, 3) it has 6 pairs in common with I_3, so that Γ^3 possesses three double tangents; so Γ^3 is of deficiency *zero* and of order *eight*.

The system (S, P) has now the symbol (4, 6); consequently $C_4{}^6$ and $\Gamma_8{}^5$ touch each other in 10 points R. Their remaining common tangents are determined by 4 double points of I_3 and the 6 coincidences of (S, S').

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Chemistry. — In the absence of Dr. J. M. VAN BEMMELEN, Prof. H. KAMERLINGH ONNES presents a paper from Dr. F. A. H. SCHREINEMAKERS entitled: "*Notes on equilibria in ternary Systems.*"

(Read March 30, 1901).

The experimental difficulties encountered in the determination of the composition of conjugate liquid phases are sometimes so great that, however desirable a knowledge of these compositions may be, the investigation of them has to be abandoned. Such cases occur for instance:

1. When the two liquids, which are in equilibrium, form an emulsion which does not separate into two phases, or does so only after an extremely long time.

2. When analytical chemistry does not provide us with the means of quantitatively determining the components.

Nothwithstanding this we may in such cases gain our object, if only approximately, and by indirect means, as I will demonstrate in what follows.

Let us take as an example the system: Water, Phenol and Acetone. A short communication on this system is to be found in the proceedings of the Academy 1899—1900 and a more full account in Zeitschr. f. Phys. Chem. 33.78. The results communicated in those papers concern the forms and positions of the connodal curves at different temperatures. To obtain these, the following course was adopted. Varying quantities of phenol were introduced into a mixture of water and acetone of known composition, obtained by direct weighing of the components, and the temperature was determined at which the two liquid phases formed passed into a single one. In this manner mixtures of water and acetone containing 1,83, 4,24, 7,94, 12,2, 15,6, 24,6, 31,8 40,3, 50,2, 59,9 and 64,9 percent of acetone were tested.

From these determinations we may easily obtain the connodal curves for different temperatures by interpolation and this method should always be applied when it is only possible to weigh the components. The difficulties mentioned in 1 and 2 are thus without influence. Table I contains the compositions of the solutions of the connodal curve at 56°.5 obtained in this way.

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TABLE I.

Compositions of the solutions of the connodal line at 56°5.

pCt	W.	85,5	89.0	89.1	86.5	82.5	79.1	67.9	59.3	48.1	36.9	26	22.7
pCt	Ac.	0	1.7	3.9	7.5	11.5	14.6	22.2	27.7	32.5	37.1	34	22.8
pCt	Ph.	14.5	9.3	7.0	6.0	6.0	6.3	9.9	13.0	19.4	26.0	40	54.5

pCt	W.	23.9	25.9	27.9	30.8	32.0	34.5	36.9	38.8	40
pCt	Ac.	16.1	12.1	9.1	5.7	4.5	3.0	1.6	0.7	0
pCt	Ph.	60.0	62.0	63.0	63.5	63.5	62.5	61.5	60.5	60

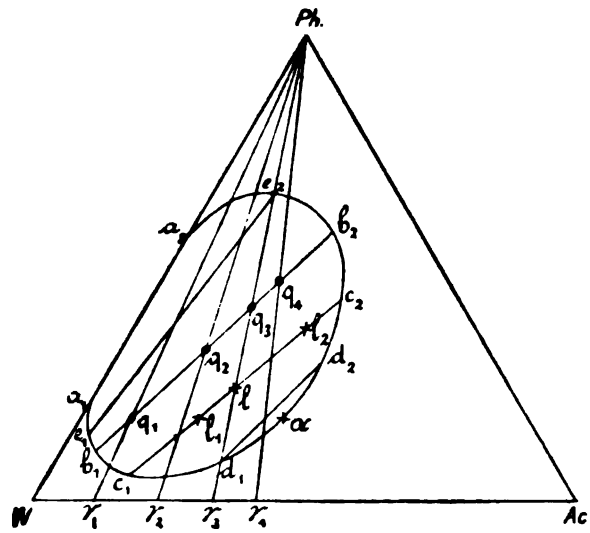

Fig. 1.

By means of table I the connodal curve for 56°5 may now be drawn; in Fig. 1 it is indicated by the curve a_1 α a_2. It is, of course, known that the liquid phase a_1 may be in equilibrium with a_2 because both are only binary liquids, but how matters are situa-

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ted as regards the ternary phases is quite unknown, as is also the position of the foldpoint α. It is known, for instance, that at the given temperature a liquid phase b_2 may be in equilibrium with another, but with *which* other is *not* known; it is also known for instance that a liquid exists which may be in equilibrium with another one; with which other, however, is as yet unknown.

If we now wish to analyse the conjugated liquid phases which occur in this system we meet with the difficulties stated in I; with certain concentrations of phenol and acetone the two layers only formed emulsions which did not separate even after waiting for hours; as we shall see, however, the top layer was present chiefly on the surface and the other at the bottom of the emulsion. In order to learn the composition of the two layers which were in equilibrium with each other, I proceeded in the following manner.

Into a small bottle, I weighed known quantities of water, acetone and phenol so that the composition of the total liquid was accurately known. Let l in fig. 1 be the point showing the composition of this mixture and c_1 and c_2 the two liquid phases into which the mixture separates at 56°5. In order to obtain equilibrium, the two layers were thoroughly shaken which caused an emulsion to form. After this had been at rest for some time a portion was removed by means of a pipette from both the top and the bottom and submitted to analysis.

The composition of the one part is indicated in the figure by l_1, that of the other by l_2 and it is natural that the three points l, l_1 and l_2 must be situated on a straight line which is to be used as a check on the analysis. If the straight line $l_1\, l\, l_2$ is now drawn and its points of intersection with the connodal curve c_1 and c_2 determined, these will then indicate the composition of the two liquid phases which are in equilibrium with each other and which constitute the emulsion. In this manner, I have determined the position of different chords of the connodal curve and therefore, also the compositions of the liquid phases which are in equilibrium at 56°5. From the determinations communicated in table 2, to which have also been added the determinations of some clear solutions, it appears that the chords have the positions approximately indicated in fig. 1. For instance b_2 lies further from the side $W.—Ph$ than b_1, c_2 further than c_1 or in other words, if we call the solution of branch $a_1\,\alpha$ the aqueous and that of $a_2\,\alpha$ the phenolic layer, acetone dissolves more readily in the phenolic than in the aqueous layer.

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TABLE II.

Composition of the conjugated solutions at 56°5.

Brauch $a_1 \alpha$.			Branch $a_2 \alpha$.		
pCt. W.	pCt. Ac.	pCt. Ph.	pCt. W.	pCt. Ac.	pCt. Ph.
88.5	0	14.5	40	0	60
88.8	1.2	10.0	29.3	7.3	63.4
89.1	3.9	7.0	230	17.1	59.4
88.62	5.28	6.1	22.5	22.8	54.7
86.7	7.3	6.0	22.5	28.0	49.5
85.5	8.5	6.0	22.9	28.8	48.3
76.0	16 9	7.1	28.6	36.1	35.3
75.1	17.5	7.4	28.8	36.3	34.9
69.5	21.5	9.0	34.0	37.5	28.5

From the foregoing it is plain how the difficulties mentioned in 1 may be got over if we can only determine quantitatively the three components or two of them. If this is also impossible, there is still at our disposal another method for determining the situation of the chords, namely determinations of vapour tensions.

Let us take, for instance, a mixture represented in figure 1 by q_1; at 56°5 this mixture will separate into the two liquid phases b_1 and b_2 possessing a certain vapour pressure. If we take a mixture q_2 this will also separate into two layers b_1 and b_2 although the relative quantities of these phases will, of course, be different. The vapour tension however, will be *the same*. This is, of course, also the case if we take mixtures like q_3 and q_4 and generally for all mixtures represented by points on the chord b_1 b_2.

All mixtures represented by points on the chord b_1 b_2 have therefore, the same vapour tension. Inversely the position of the chord may be determined when the compositions of different mixtures having the same vapour tensions at the same temperature are known.

In the system: water-acetone-phenol I have made many determinations of vapour tension which I hope to communicate more fully, later on; I will now mention only a few of the determinations and

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show how the position of the chords may be determined from them. The vapour tension of each of the mixtures investigated has been determined at 10 to 15 different temperatures; in what follows I only mention the vapour tensions at 56°5 which have been obtained from these determinations by interpolation.

Let us first consider the side *W-Ph* of fig. 1, that is mixtures which contain only water and phenol.

TABLE 3.

Vapour tensions at 56°5.

0% *Ac.*

% Ph.	0.	2.0	5.58	7.42	10.88	14.5	60.0	69.2	76.7	80.34	88.06
P in m.M.	125	125	127	127	127	126	126	124	122	118	102

7.94% *Ac.*

% Ph.	0	1.22	2.41	5.93	10.02	15.19	19.81	29.93	40.48	49.28	62.67	70.15	74.25	80.76
P in m.M.	278	271	262	236	216	193	180	158	147	140	135	130	126	119

15.6% *Ac.*

% Ph.	0	1.39	3.03	6.14	9.63	14.30	19.81	29.74	38.81
P in m.M.	387	369	350	318	292	262	232	193	171
% Ph.	49.60	60.13	66.98	74.88	83.00				
P in m.M.	155	144	137	130	115				

22.52% *Ac.*

% Ph.	0	3.08	8.38	13.95	20.01	24.38	29.72	35.95
P in m.M.	446	408	359	318	277	253	226	205
% Ph.	41.69	49.51	59.49	69.29	79.68.			
P in m.M.	186	167	155	140	122.			

31.82% *Ac.*

% Ph.	0	4.10	7.68	13.36	20.13	24.77	29.99	34.13	39.29
P in mM.	524	468	428	379	335	302	274	251,5	224
% Ph.	40.93	45.57	51.48	57.64	62.96	71.06	79.77		
P in m.M.	218	202	186	170	160	141	123.		

The vapour tensions are given in table 3 under 0 pCt. of acetone. It will be seen that as the quantity of phenol increases, the pressure first rises from 125—127 m.m., falling again to 126 m.m. when the liquid contains 14.5 per cent of phenol. If more phenol is added, two liquid phases appear and the pressure remains 126 m.m. until the mixture contains 60 per cent of phenol; if still more phenol is added, there only remains one liquid phase and the vapour tension

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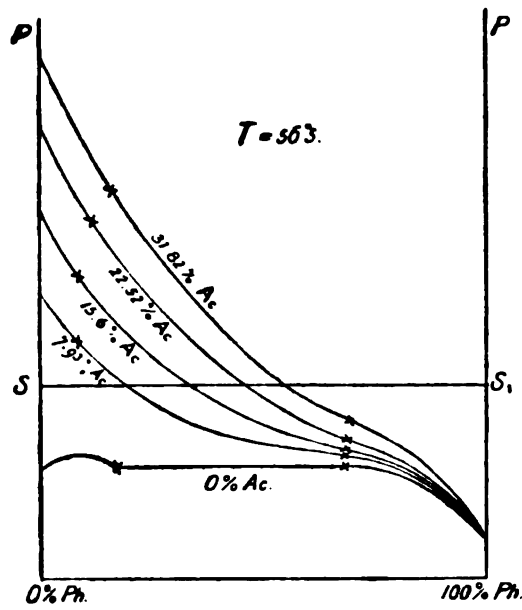

Fig. 2

decreases continuously. This is represented in the usual way in fig. 2. The amount of phenol is given on the horizontal and the pressure on the vertical axis. A line is thus obtained which is indicated diagrammatically by the one marked 0 pCt. of acetone. At the left hand side A consist of a part with a maximum, in the centre, where both liquid phases occur, of a horizontal part and for the remainder of a slanting line. Passing now, in fig. 1, along the side W—Ph from W to Ph, the pressure at first increases, reaches a maximum and then decreases until a_1 in reached; from a_1 to a_2 the pressure remains constant and from a_2 to Ph it again decreases; the pressure therefore remains constant in the region in which two liquid phases are present.

It is different, however, if we move along a line through the triangle, for instance from r_3 to Ph, along the line $r_3\,Ph$; from r_3 to d_1 we then move in the homogenous field; from d_1 to e_2 we traverse the heterogenous and from e_2 to Ph we find ourselves again in the homogenous field. It is, of course, plain that if we move over the parts $r_3\,d_1$ and $e_2\,Ph$ the pressure will be continually altering, as was the case with the parts Wa_1 and $a_2\,Ph$; on the part $d_1\,e_2$, the behaviour is, however, different from that on $a_1\,a_2$. On the part $a_1\,a_2$ the vapour tension remains unchanged; on $d_1\,e_2$ it changes continuously. This will be easily unterstood if we reflect that the pressure at d_1 is the same as the pressure of the two conjugated phases $d_1 + d_2$; at l the vapour pressure is that of the system $c_1 + c_2$; in q_3 the vapour pressure corresponds to that of the system $b_1 + b_2$; in e_2 the vapour pressure is the same as that of the system $e_1 + e_2$. We therefore see that if we move from d_1 to e_2 the vapour pressure must be changing continually just as it alters along the connodal line from d_1 to e_1 or from d_2 to e_2. From the determinations it follows that the vapour pressure increases along the connodal line from a_1 and a_2 in the direction of the foldpoint α.

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If, therefore, we move from d_1 to e_2 we must notice a continual decrease of the vapour pressure.

All the solutions situated on the line r_3 *Ph* have the peculiarity that the relation between water and acetone is the same in all of them. The vapour tensions of the solutions on this line may therefore be represented as though we had a binary mixture of the components of which one is phenol and the other a mixture of water and acetone in constant proportion. We, therefore, put down in figure 2 the amount of phenol on the horizontal and the pressure on the vertical axis. Let us take as example the solutions in which the relation between water and acetone is 84.4 : 15.6 or in other words those which contain 15.6 percent of acetone if we disregard the presence of the phenol. These determinations are given in table 3 marked 15.6 percent acetone. Under *P* the vapour pressure in m.m. is given and under pCt. *Ph* the total amount of phenol in the liquids. The first determination, therefore, gives the vapour tension of a mixture which contains no phenol, that is of a mixture of water and acetone containing 15.6 percent of acetone. As may be plainly seen from this series, the vapour pressure decreases continually with increasing quantities of phenol.

In fig. 2 this series is indicated by the curve marked 15,6; the curve is not continued to its endpoint, 100 percent of phenol, but only to 83 percent. It must, of course, end at the same point as the line indicating the vapour tension of water and phenol only.

In table 3 some other determinations are given under 7.94, 22.52 and 31.82 percent acetone, the significance of which will be sufficiently apparent after the foregoing explanation. The corresponding vapour pressure curves in fig. 2 are marked by the same figures. Each of these curves consists of three parts, namely the two portions at the sides which relate to the homogenous liquids and the portion in the middle (between the two crosses) which relates to the mixtures which separate into two liquid phases on the connodal curve. In the two points where these three meet, they exhibit a discontinuity.

From fig. 2 the situation of the chords of the connodal curve at 56°.5 may be obtained.

Let us draw an horizontal line ss_1 which intersects some of the vapour tension curves; each point of intersection indicates a solution or a complex; all the solutions and complexes situated on this line have the same vapour tension. Let us confine ourselves to the complexes only or to those parts of the vapour tension curves, which are indicated in figure 1 by points within the connodal curve and therefore belong to the heterogenous field. Let us draw the line

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ss_1 in such a way that it indicates for instance a vapour tension of 180 m m. We then have 4 complexes, indicated on the curves by 7.94, 15.6, 22.52 and 31.82 percent acetone, which at 56°.5 have a vapour pressuie of 180 m.m. and must therefore in fig. 1 be situated on the same chord as for instance the points q_1, q_2, q_3 and q_4.

The composition of these complexes may be ascertained from fig. 2; from the figure we may obtain the amount of phenol in the complex, whilst the relation between the other two components, that is between water and acetone, is known. Thus it is found, for instance, that the point of intersection of the line ss_1 with the vapour tension curve of 15.6 percent acetone indicates an amount of phenol of 34.6 percent. The complex, therefore, contains $100 - 34.6 = 65.4$ percent of water and acetone of which $\frac{15.6}{100} \times 65.4$ percent is acetone and $\frac{84.4}{100} \times 65.4$ percent is water. We, therefore, find that this complex consists of 55.2 percent of water, 10.2 percent of acetone and 34.6 percent of phenol. In the same manner, the composition of the complexes, indicated by the other parts of intersection may be calculated.

In the foregoing, we have drawn the line ss_1 in such a manner that it indicated a vapour tension of 180 m.m.; this vapour tension may, of course, be taken differently; we then obtain other points of intersection and consequently other complexes and also other chords. In table 4 a few results of these calculations are given for 180, 220, 260 and 300 m.m.

TABLE 4.

Temperature 56°5.

Composition of the complexes with a vapour pressure of 180 m.m.

pCt. W.	pCt. Ac.	pCt. Ph.
73.8	6.4	19.8
55.2	10.2	34.6
43.4	12.6	44.0
31.6	14.8	53.6

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Composition of the complexes with a vapour pressure of 220 m.m.

pCt. W.	pCt. Ac.	pCt. Ph.
83.7	7.3	9.0
65.3	12.1	22.6
53.0	15.4	31.6
40.7	18.9	40.4

Composition of the complexes with a vapour pressure of 260 m.m.

pCt. W.	pCt. Ac.	pCt. Ph.
72.2	13.3	14.5
59.7	17.3	23.0
46.1	21.5	32.4

Composition of the complexes with a vapour pressure of 300 m.M.

pCt. W.	pCt. Ac.	pCt. Ph.
77.3	14.3	8.4
64.7	18.8	16.5
51.2	23.8	25.0

Let us first take the 4 complexes which at 56°.5 have a vapour tension of 180 m.m.; if these are placed in the triangle it will be seen, that they are situated on a straight line; the same is the case with the 4 complexes with a vapour pressure of 260 m.m. and also with the three complexes whose vapour pressure amounts to 300 m.m.

We have, therefore, again found four chords; for the determination of each of these, of course, only two points were needed; the others only serve as a check to control the accuracy obtained.

It is worthy of attention that the chords derived from table 4 are, theoretically, not altogether comparable with those from table 2; the latter belong to a connodal line at 56°.5 at a constant pressure, the former, to a connodal line at 56°.5 at *its own* vapour pressure. As however, a small change in the pressure has generally a very small influence on the composition of the two liquid phases in equilibrium, the chords determined in the two ways are practically

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comparable. That this is the case is seen when the chords obtained from the figures given in the two tables are set out in the triangular diagram.

An examination of figure 2 reveals some further peculiarities which may be explained. From the vapour tension curve, marked 0 percent acetone, it is seen that the vapour tension of water is increased by the addition of small quantities of phenol. I have already shown in a former article that this is in accordance with the formula of VAN DER WAALS which applies in this case. But if we add phenol to a water-acetone mixture it is different, for, if we take mixtures of water and acetone containing 7.93, 15.6, 22.52 or 31.82 percent of acetone, we notice from the corresponding vapour tension curves in fig 2 that the vapour pressure falls. The question is now whether the addition of a new substance to a binary mixture has the same influence as the addition of the same to a simple liquid. As I will show this is by no means the case.

We take for example a liquid of the composition

$$1\ Mol\ A \quad x_1\ Mol\ B \quad y_1\ Mol\ C.$$

which is in equilibrium with a vapour of the composition

$$1\ Mol\ A \quad x\ Mol\ B \quad y\ Mol\ C.$$

Let us call the thermodynamic potential, the entropy and the volume of this liquid ζ_1, η_1 and V_1 and that of the vapour phase ζ, η and V.

In equilibrium we have:

$$\left.\begin{aligned} \zeta_1 - x_1\frac{\partial\zeta_1}{\partial x_1} - y_1\frac{\partial\zeta_1}{\partial y_1} &= \zeta - x\frac{\partial\zeta}{\partial x} - y\frac{\partial\zeta}{\partial y} \\ \frac{\partial\zeta_1}{\partial x_1} = \frac{\partial\zeta}{\partial x} \qquad \frac{\partial\zeta_1}{\partial y_1} &= \frac{\partial\zeta}{\partial y} \end{aligned}\right\} \quad \ldots \quad (I)$$

Assuming that the relative quantities of the components A and B is kept constant in the liquid, x_1 is also constant. If we also keep the temperature constant the only variable quantities remaining are y_1 x y and P. From the equations (I) we obtain:

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$$\left.\begin{aligned} -(s_1 x_1 + t_1 y_1)\,dy_1 + \left(V_1 - x_1\frac{\partial V_1}{\partial x_1} - y_1\frac{\partial V_1}{\partial y_1}\right)dp = \\ = -(rx + sy)\,dx - (sx + ty)\,dy + \left(V - x\frac{\partial V}{\partial x} - y\frac{\partial V}{\partial y}\right)dp \\ s_1\,dy_1 + \frac{\partial V_1}{\partial x_1}\,dp = r\,dx + s\,dy + \frac{\partial V}{\partial x}\,dp \\ t_1\,dy_1 + \frac{\partial V_1}{\partial y_1}\,dp = s\,dx + t\,dy + \frac{\partial V}{\partial y}\,dp \end{aligned}\right\} \quad \text{(II)}$$

in which

$$s_1 = \frac{\partial^2 \zeta_1}{\partial x_1\,\partial y_1} \quad t_1 = \frac{\partial^2 \zeta_1}{\partial y_1^2} \quad r = \frac{\partial^2 \zeta}{\partial x^2} \quad s = \frac{\partial^2 \zeta}{\partial x\,\partial y} \quad t = \frac{\partial^2 \zeta}{\partial y^2}$$

If we multiply the second equation by x and the third by y and add the results to the first we find:

$$[s_1(x-x_1) + t_1(y-y_1)]\,dy_1 + \left[V_1 + (x-x_1)\frac{\partial V_1}{\partial x_1} + (y-y_1)\frac{\partial V_1}{\partial y_1}\right]dp = V\,dp$$

$$\frac{dp}{dy_1} = \frac{s_1(x-x_1) + t_1(y-y_1)}{V - V_1 + (x_1 - x)\dfrac{\partial V_1}{\partial x_1} + (y_1 - y)\dfrac{\partial V_1}{\partial y_1}} \quad \text{(III)}$$

This equation shows the change in pressure which occurs when we add new substance to a liquid made up of the components A and B. Let us assume that the quantity y_1 of the new substance is exceedingly small so that y is also very small. We then find for the limit value [1]):

$$t_1 = \frac{RT}{y_1}$$

Formula III now becomes:

$$\frac{dp}{dy_1} = \frac{s_1(x-x_1) + RT\left(\dfrac{y}{y_1} - 1\right)}{V - V_1 + (x_1 - x)\dfrac{\partial V_1}{\partial x_1}} \quad \text{(IV)}$$

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[1]) Zeitschr. für Phys. Chem. 25, 327.

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which may, therefore, be applied when only small quantities of the new substance are added. As will be readily understood, the sign of the denominator is always positive; as to the sign of the numerator, this cannot be judged without further information. The quantity $\frac{y}{y_1}$ is the partition coefficient of the new substance between vapour and liquid. This coefficient decides whether, on adding a new substance to a simple liquid, an increase or decrease of P will take place; this, however, is by no means the case here, as there is, in addition, another term $s_1(x-x_1)$ which may be either positive or negative.

The value of $\frac{dp}{dy_1}$ from IV may also be considered as a function of x_1, that is of the composition of the binary mixture to which the new substance is added. It may, therefore, happen that if x_1 is allowed to vary within wide limits, $\frac{dp}{dy_1}$ may change sign.

We, therefore, come to the following conclusion:

„if we add a new substance to a binary mixture, either an „increase or a decrease of the vapour tension may take place accor- „ding to the composition of the binary mixture."

This is in accordance with observations made on the system water, acetone and phenol. If we take water and add phenol to it the vapour pressure increases (see fig. 2). This is also the case when, instead of pure water, we use water containing but little acetone. If, however, we use mixtures containing 7.94 or more of acetone a decrease of vapour tension will be noticed as shown in fig. 2.

The difference between the behaviour of a single substance and of a binary mixture is even more evident when the addition af a new substance, which does not appear in the vapour phase, is considered.

In formule IV we must then put $y = 0$ and we obtain:

$$\frac{dp}{dy_1} = \frac{s_1(x-x_1) - RT}{V - V_1 + (x_1-x)\frac{dV_1}{dx_1}} \quad \ldots\ldots\ldots \quad (V)$$

The numerator of this fraction may now be either positive or negative so that we come to the following conclusion:

„if we add to a binary mixture new substance not passing

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„into the vapour, the vapour tension may be either increased or „decreased."

We, therefore find an important deviation from the law of decrease of vapour tension in the case of simple substances. Let us assume that the binary mixture has a maximum or minimum vapour pressure. We then must put $x = x_1$, causing the term $s_1 (x - x_1)$, to disappear from the formula; $\frac{dp}{dy}$ will consequently be negative so that we find that:

„if we add to a binary mixture with a maximum or minimum „vapour pressure a new substance, which does not pass into the „vapour, pressure is decreased."

We, therefore, come to the conclusion that the law of the decrease of vapour pressure for a simple liquid is still applicable to a binary mixture with a maximum or minimum vapour pressure, but that in general either an increase or a decrease of vapour pressure may occur with binary mixtures.

When calculating the formula II from I we have taken the pressure as variable and the temperature as constant. If we now take the pressure as constant and the temperature as variable we find in a similar manner that:

„if we add to a binary mixture a new substance which does not pass into the vapour, the boiling point may be either increased or decreased. Only binary mixtures with a maximum or minimum boiling point obey the ordinary law of increase of boiling point for simple substances."

In the equilibria of the system water, ethylalcohol and sodium carbonate investigated in our laboratory by Mr. KETNER, we also meet with an example of the deviations which binary mixtures show on adding a third substance, in contrast to simple substances.

The boiling point of water rises when sodium carbonate is added to it; if however, we take mixtures of water and alkohol, the boiling point is depressed by the addition of this salt, provided that the amount of alcohol in the mixture exceeds a certain limit. The determinations are given in table V. As will be seen these determinations have been made for alcoholic mixtures containing:

0, 1.2, 2.2, 5.0, 9.8, 21.3, 35.6, 45.4 and 55.0 percent of alkohol.

Under percentage of salt are given the quantity of added $Na_2 CO_3$ to 100 parts of the water-alcohol mixture; under ΔT the change in

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the boiling point, the sign + indicating the increase and — the decrease of the boiling point.

TABLE V.

Change in the boiling point of water-alcoholmixtures on addition of Na_2CO_3.

0 % Alcohol.		1.2 % Alcohol.		2.2 % Alcohol.	
% salt	Δ T	% salt	Δ T	% salt	Δ T
0.65	+ 0°.10	0.80	+ 0.05	0.44	+ 0.01
1.62	+ 0°.21	1.79	+ 0.13	0.91	+ 0.01
		2.57	+ 0.16	1.75	+ 0.03
		3.38	+ 0.20	2.52	0.00

5.0 % Alcohol		9.8 % Alcohol		21.3 % Alcohol.	
% salt	Δ T	% salt	Δ T	% salt	Δ T
0.48	—0.04	0.67	—0.02	0.61	—0.14
1.31	—0.07	1.33	—0.12	1.04	—0.27
2.15	—0.14	2.02	—0.22	1.72	—0.46
		2.67	—0.30	2.37	—0.66
				3.23	—0.91

35.6 % Alcohol		45.4 % Alcohol		55.0 % Alcohol	
% salt	Δ T	% salt	Δ T	% salt	Δ T
0.52	—0.14	0.43	—0.08	0.16	—0.03
1.06	—0.29	0.84	—0.16	0.60	—0.15
1.62	—0.45	1.45	—0.31	1.19	—0.25
		2.09	—0.42	1.80	—0.35
		2.63	—0.52		

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Chemistry. — Dr. P. K. LULOFS: "*Substitution velocity in the case of aromatic halogen-nitroderivatives.*" (Communicated by Prof. LOBRY DE BRUYN).

(Read March 30, 1901).

Some two years ago Dr. ALPH. STEGER made an investigation of the velocity of the substitution of oxymethyl and oxyethyl for the nitro-group in ortho- and paradinitrobenzene [1]). This research included the influence exercised by a change of temperature, decrease of concentration, addition of a substance with a common ion and the regulated addition of water to the alcohol.

It now became important to extend this investigation to other substances. After preliminary experiments with various compounds, Dr. LULOFS has in the first place confined himself to chloro-, bromo- and iododinitrobenzene 1. 2. 4. Of these compounds it had been long since established that the halogen atom is liable to all kinds of substitution for instance by alkalis, ammonia, amines, alcoholates etc. It now appeared that the reaction with the last named substances lends itself very well to a quantitative research and for this reason sodium methoxide and sodium ethoxide were again chosen here.

As a first result it was established that the chlorine atom is much more easily replaced by oxymethyl or oxyethyl than the nitro-group in ortho- and paradinitrobenzene. It was further confirmed that of the three halogens the chlorine is the most and the iodine the least readily replaced by oxyalkyl; this had already been observed by KÖRNER by comparing the periods in which the reaction is ended. The constants for the reaction of the three halogen compounds with sodium ethoxide in absolute alcohol at the same concentrations are in the proportion of 3.26 : 2.03 : 0.455 (temp. 15°). It is remarkable that in the case of the aliphatic halogen compounds the behaviour of the halogens is just the reverse; in these compounds the iodine is in the weakest and the chlorine in the strongest combination with the carbon atom.

In the second place Dr. LULOFS studied the influence of the decrease of concentration on the constant. It had been proved by Dr. STEGER that the reaction between orthodinitrobenzene is not influenced by dilution. On the other hand CONRAD and BRÜCKNER [2]) had found that during the formation of an ether from an alkyl iodide and an alcoholate, this influence most decidedly exists in this sense that the reaction-constant increases with dilution.

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[1]) Rep. Meeting 29 Oct. 1898; Dissertation 1898 and Recueil 18, 13.

[2]) Z. phys. Chem. 5. 289. This result was confirmed by STEGER (l. c.).

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This last result, as we know, agrees with the electrolytic dissociation theory and may, therefore, be used in support of the view that the formation of ether is due to an ion-reaction. We are therefore confronted by the remarkable fact that the first reaction is not influenced by dilution whilst the second is affected by it, so that the second only should be considered as a reaction between ions.

In the reactions investigated by Dr. LULOFS, the reaction-constant is found to increase (as in the case of ether formation) with dilution and particularly when ethyl alcohol is used. In the case of chlorodinitrobenzene, the constant rises from 2.94 (gasconcentration) to 3.56 (one-fifth of that concentration); under the same circumstances the constant of the bromo-compound rises from 1.88 to 2.33.

It is a peculiar fact that the rise is much less marked when using sodium methoxide in methyl alkohol, being from 1.10 to 1.18 in the case of the chloro-compound.

In the third place, some experiments were made by Dr. LULOFS on the influence of the addition of a common (Na) ion. Dr. STEGER (l. c.) had found that this influence does not exist in the case of the reaction with orthodinitrobenzene, but that in the formation of ethers it is well marked, producing, in accordance with the electrolytic dissociation theory, a diminution of the reaction-constant. In the present case agreement with the last reaction was observed; for instance an addition of sodium bromide to the mixture of bromodinitrobenzene and sodium ethoxide caused a decided lowering of the constant.

We therefore see that in this case as well as in the case of dilution, the aromatic nitrohalogen compounds behave like the aliphatic halogen derivatives. The totally different behaviour of orthodinitrobenzene in an otherwise quite analogous reaction remains unexplained.

In the fourth place it was ascertained in what manner the reaction coefficients depended on the addition of water to the two alcohols. The reaction with orthodinitrobenzene and those in which ethers are formed had previously yielded very interesting results in this respect. [1]) Dr. LULOFS was in a position to show that chloro- and bromodinitrobenzene behaved in the same way. The coefficients remained constant even for an alcohol mixture containing 40 percent of water. In dilute ethylalcohol they decrease with the increase of the amount of water; on the other hand when dilute methyl alcohol is used they

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[1]) LOBRY DE BRUYN and A. STEGER. Proc. 30 Sept. 1899. Recueil **18, 41, 311.**

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first increase, then remain constant and finally decrease when the amount of water reaches about 40 percent. When using alcohol-water mixtures as solvent, it appeared that the decrease in concentration causes a rise and the addition of a substance with a common ion a lowering of the constant.

Dr. LULOFS research [1]), which may be usefully extended in various directions, points, like the results quoted, to the desirability of a study of the conductivity of the alcoholates when dissolved in the pure alcohols (partly carried out by CARRARA) or in mixtures of alcohol and water. It will then be possible to ascertain whether there exists a parallellism between the change of the reaction-constants and that of the conductivity.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS: *„On the progressive change of the factor i as function of the concentration."*

(Read March 30, 1901).

Of the salts, which I have already investigated, KNO_3 [2]) is the only one for which the factor *i* decreases with increasing concentration. It, therefore, seemed to me very interesting to ascertain whether other nitrates behave similarly.

KNO_3 being an anhydrous salt, I purposely chose nitrates of which no hydrates are known.

In this investigation I have availed myself of my improved Landsberger apparatus [3]), which is sufficiently accurate for my purpose.

Before proceeding to mention the results, I will first draw attention to some points to which attention should be paid in the determination of boiling points by this method.

In determining the boiling point of pure water, it is noticed that the boiling point continuously rises during the progress of the experiment. In my apparatus this rise amounted 0.01^0 in 25 minutes. The explanation of this phenomenon is found in the continual increase in height of the column of water in consequence of the condensation of the aqueous vapour, which takes place. When the column of water increases in height, the pressure and consequently

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[1]) Further particulars in his dissertation, Amsterdam, 1901.

[2]) Proc. 21 April 1900 714.

[3]) Proc. 26 May 1900 31.

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the boiling point is raised. As I wished to make up solutions of different concentrations by adding to the water (of which I had determined the boiling point) some salt thereby causing an increase in the height of the column, it was necessary to know the increase of temperature, which corresponded to a certain increase in the height of the column of liquid.

I, therefore, conducted a series of boiling point determinations of pure water in which the height of the liquid was varied. In this way I found, that an increase of 10 m.m. in the height of the column corresponded with a rise of 0.01° in the temperature.

Theory requires for 10 m.m. water at 100° an increase of the boiling point about thrice as large. The explanation of this difference must be looked for in the vigorous mixing, which occurs in the boiling liquid owing to which, as will be readily understood, the theoretical increase cannot be obtained. As the degree of mixing is moreover dependent on the relation between the amount of steam transmitted in unit time and the volume of the boiling liquid, the observed rise in temperature will depend on the dimensions of the apparatus and the method of working. That a fairly complete mixing took place in my apparatus was proved by an investigation of the temperature of the different liquid layers. This investigation originated in the following phenomenon. I happened to find that, when the thermometer inside the liquid was raised or lowered to the extent of 1 c.m., a change of 0.005° was noticed in the temperature. Was this to be considered as a proof that the temperature of the different liquid layers was unequal, or must the explanation be found in the change of the height of the column of liquid caused by the altered position of the thermometer?

This question was decided by first ascertaining the influence of a certain increase in the height of the column of water while leaving the position of the thermometer unchanged and then repeating the experiment taking care, that the thermometer before and after the addition of water reached to the same depth. Both determinations gave exactly the same result from which follows, that the temperature of the different layers of water of the strongly moving boiling column of liquid is the same and that, therefore, the small increase of temperature of 0.005° was caused by the change in the height of the column of liquid already mentioned. From the foregoing it appears that an increase in the height of the column of boiling liquid exercises an influence which cannot be neglected, so that it is necessary to find out by measurement of the increase of height, whether or not on addition of salt a correction ought to be applied.

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RESULTS.

$NaNO_3$.

Concentration in gr. mol. per 1000 gr. H_2O.	Increase of the boiling point of the solution.	Mol. increase of the boiling point.	i
0.0462	0.044°	9.516	1.83
0.0852	0.080°	9.389	1.81
0.4148	0.393°	8.948	1.72
0.8630	0.771°	8.876	1.71

$Ba(NO_3)_2$.

0.0461	0.070°	15.190	2.92
0.0868	0.104°	12.103	2.33
0.4233	0.466°	11.009	2.12
0.8890	0.911°	10.248	1.97

$Sr(NO_3)_2$.

0.0429	0.050°	11.664	2.24
0.0848	0.098°	11.561	2.22
0.4142	0.493°	11.903	2.29
0.9005	1.094°	12.148	2.34

$AgNO_3$.

0.0473	0.044°	9.294	1.79
0.0908	0.087°	9.246	1.78
0.4409	0.382°	8.665	1.67
0.9146	0.741°	8.102	1.56

$Pb(NO_3)_2$

0.0474	0.070°	14.760	2.84
0.0869	0.090°	10.351	1.99
0.4174	0.418°	10.014	1.93
0.8793	0.824°	9.371	1.80

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These tables show that while the factor i for $NaNO_3$, $Ba(NO_3)_2$, $AgNO_3$ and $Pb(NO_3)_2$ diminishes perceptibly with the increase of the concentration, it takes in the case of $Sr(NO_3)_2$ a course, which quite agrees with that observed with K Cl and Na Cl.

Although five out of the six anhydrous nitrates investigated gave the same result, the exception, noticed in the case of $Sr(NO_3)_2$, shows that the fact, that a salt is anhydrous or not anhydrous, has no definite influence on the progressive change of i.

Let us now consider what is to be learned from the determinations of the electrolytic conductivity of solutions of the salts K Cl, KNO_3, Na Cl and $NaNO_3$.

KRANNHALS [1]) found at 99°.4 the following:

K Cl ($\mu_\infty = 348$) [2]).

Concentration	Mol. conductive power μ.	% increase of $\frac{\mu}{\mu_\infty}$ in the concentration interval 1—$^1/_{16}$ gr. mol.	i	% increase of i in the concentration interval 1—$^1/_{16}$ gr mol.
1	240.0	29	1.69	11.9
$^1/_{16}$	309.9		1.89	

K NO_3 ($\mu_\infty = 340$).

1	205.8	38.5	1.605	14.6
$^1/_{16}$	285.1		1.84	

Na Cl ($\mu_\infty = 316$).

1	204.4	31.1	1.65	12.1
$^1/_{16}$	268.1		1.85	

Na NO_3 ($\mu_\infty = 309$).

1	173.7	45.4	1.56	16.6
$^1/_{16}$	252.5		1.82	

[1]) Zeitschr. f. Physik. Chem. 5, S. 250 (1890).

[2]) Instead of μ_∞ here is taken μ_{1000}, but it is easy to demonstrate, that for our purpose this manner of acting is permitted.

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In these tables it is assumed, that for the concentration given the quotient $\frac{\mu}{\mu_\infty}$ represents the degree of dissociation.

It appears, however, from JAHN's investigation that this is not the case even for very small concentrations.

The mobility of the K and Na ions appears to increase very perceptibly with the concentration, so that for liquids, which are not excessively dilute, $\frac{\mu}{\mu_\infty}$ is greater than the degree of dissociation, while the difference is continually increasing with the concentration.

All the values of i occurring in this table ought, therefore to be diminished by a certain amount which should reach a maximum for the greatest concentration.

If we now started from the supposition that the corrections, which ought to be applied in the case of the above mentioned salts in order to get the true degree of dissociation, exercise about the same influence on the progressive change of i, it would follow from this table that in the case of KNO_3 and $NaNO_3$ the degree of dissociation and consequently the theoretical value of i (from the conductivity) diminishes much more rapidly with the increase of the concentration than in the case of KCl and NaCl [2]).

Should this be confirmed by more accurate determinations of the degree of dissociation of more concentrated solutions it might provide an explanation of the fact, that the experimental i (from the decrease of vapour tension and increase of boiling point) increases with the concentration in the case of not very diluted solutions of KCl and NaCl whereas the reverse happens with KNO_3 and $NaNO_3$.

The change of the experimental i is due not only to the change of the dissociation, but also to the influence of the deviation from the diluted condition. Researches on non-electrolytes render it probable that this last influence will cause the experimental i to increase with the concentration and will, therefore, possess a sign opposite to that of the influence of the dissociation change.

As one of the influences increases the experimental values of i and the other one tends to reduce them, the final result will depend on the relative magnitudes of the two influences.

If then the dissociation in the case of one salt diminishes much

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[1]) Zeitschr. f. Physik. Chem. 33, 545 (1900).

[2]) The corrections cannot as yet be deduced from JAHN's research, as these have been determined for greater dilutions only.

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less rapidly with an increase of the concentration than in the case of another salt, it is possible that, while in the one case a very slow increase of the experimental i is observed (K Cl, Na Cl), the reverse may be the case with the other ($K NO_3$, $Na NO_3$).

In conclusion it may be remarked that the results of the freezing point determinations of not very dilute solutions have not been discussed in this paper because some doubt has been thrown on them by their disagreeing with those obtained by the determination of the vapour tensions and boiling points.

Amsterdam, Chem. Lab. University, March 1901.

(May 18, 1901).

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